# Electronic Supplementary Information

## Multi-Centered Solid-Phase Quasi-Intramolecular Redox Reactions of [(Chlorido)Pentaamminecobalt(III)] Permanganate—An Easy Route to Prepare Phase Pure $CoMn_2O_4$ Spinel

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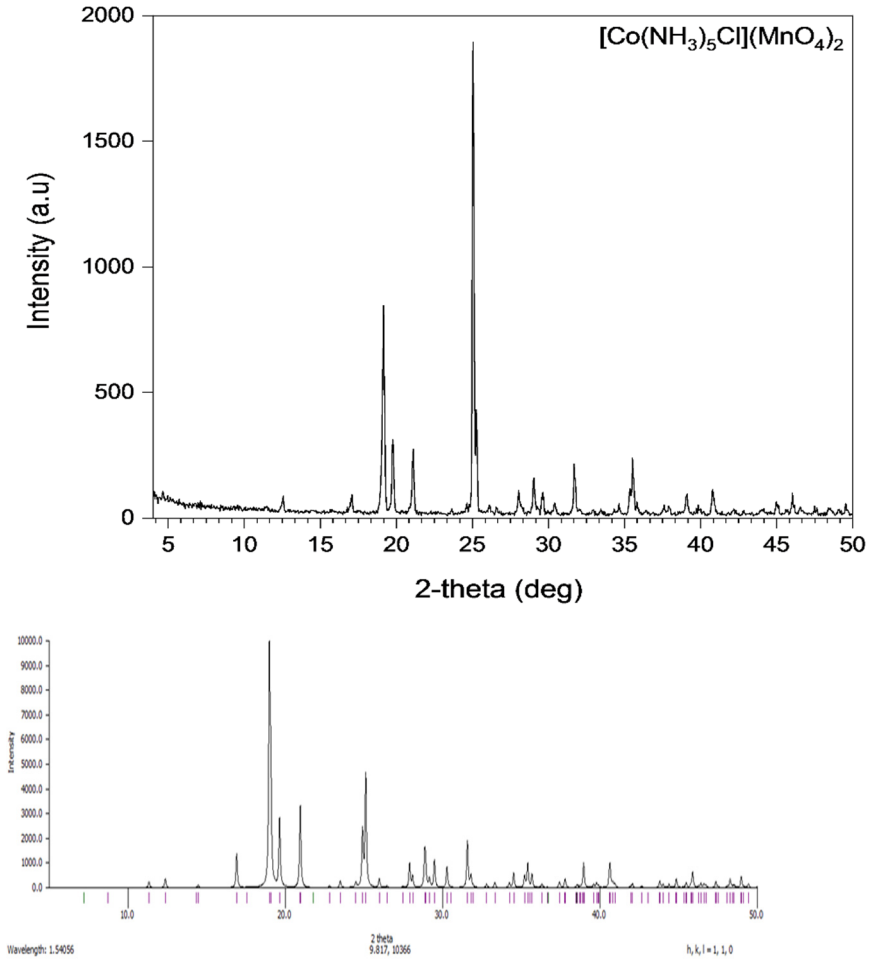





**Figure S1.** Comparison of experimental powder X-ray diffractogram and calculated one (from data of single crystal measurement) of **compound 3-Mn**.

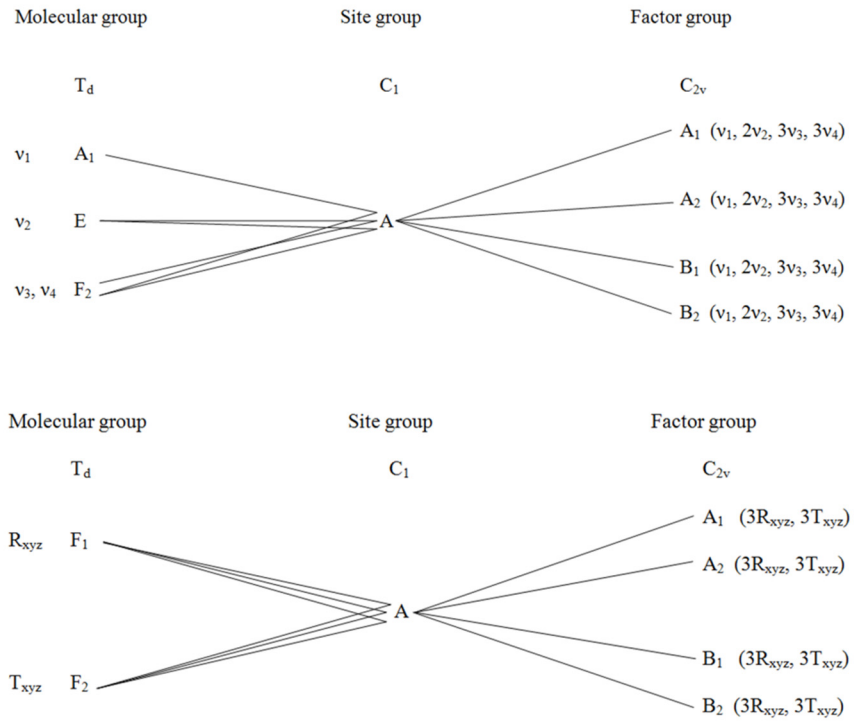



**Figure S2.** Correlation analysis for the internal and external vibrations of permanganate ion in **compound 3-Mn**.

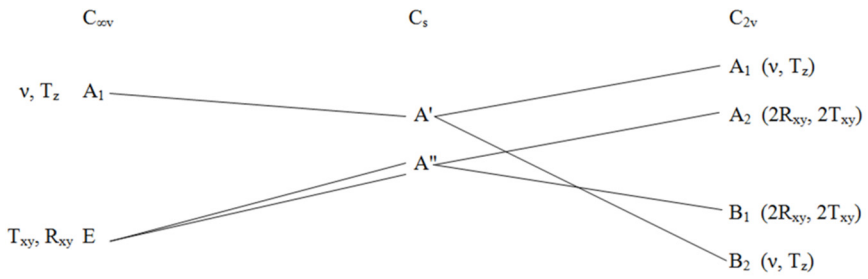



**Figure S3.** Correlation analysis for the internal and external vibrations of Co-Cl groups (molecular symmetry $C_{\infty v}$) in **compound 3-Mn.**

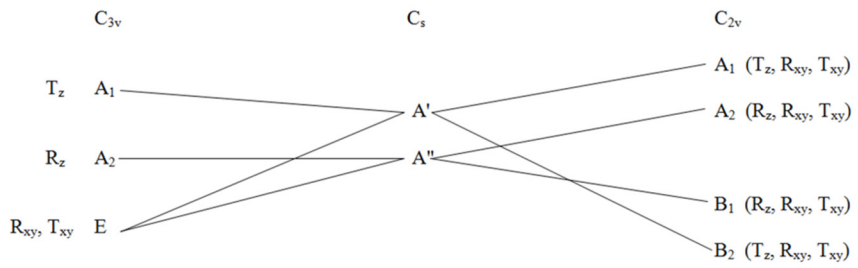



**Figure S4.** Correlation analysis for the external vibrations of ammonia ligands in **compound 3-Mn.**

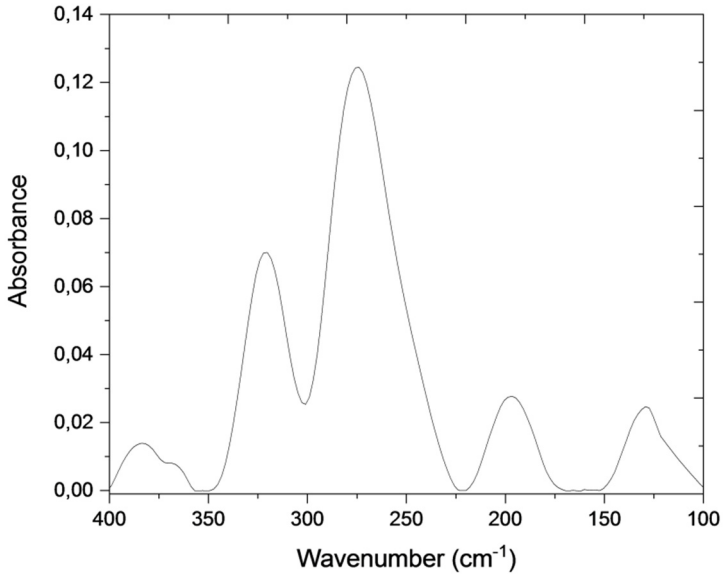



**Figure S5.** Far-IR spectrum of **compound 3-Mn** in the range of 400-100 $cm^{-1}$ at room temperature.

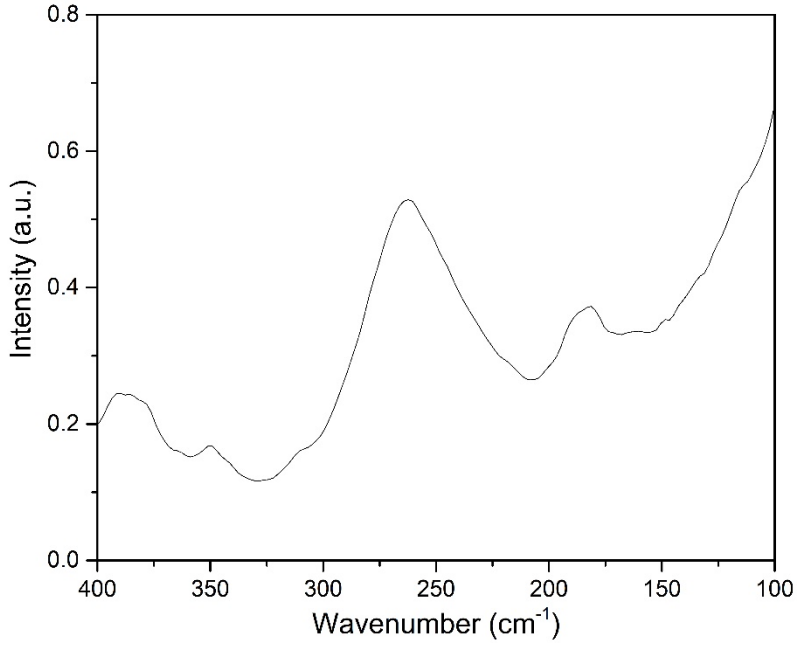



**Figure S6.** Far-IR spectrum of the deuterated **compound 3-Mn** in the range of 400-100 $cm^{-1}$ at room temperature.

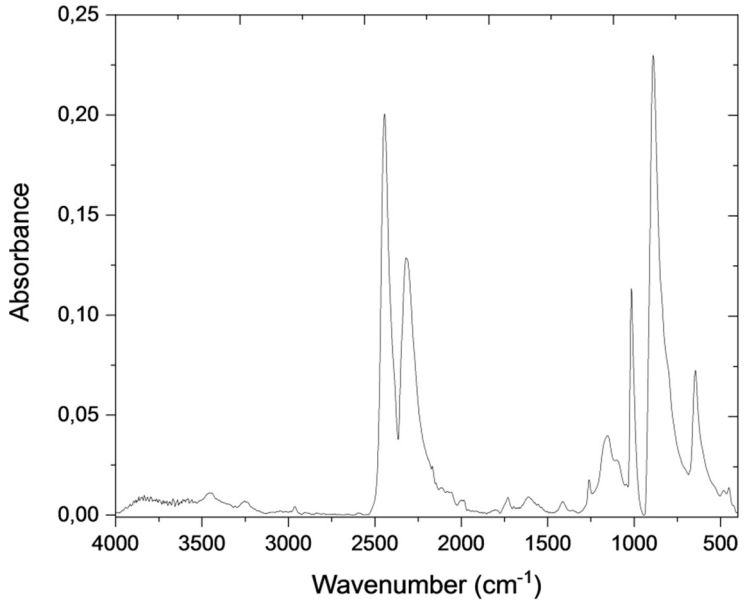



**Figure S7.** IR spectrum of the deuterated **compound 3-Mn** in the range of 4000-400 $cm^{-1}$ at room temperature.

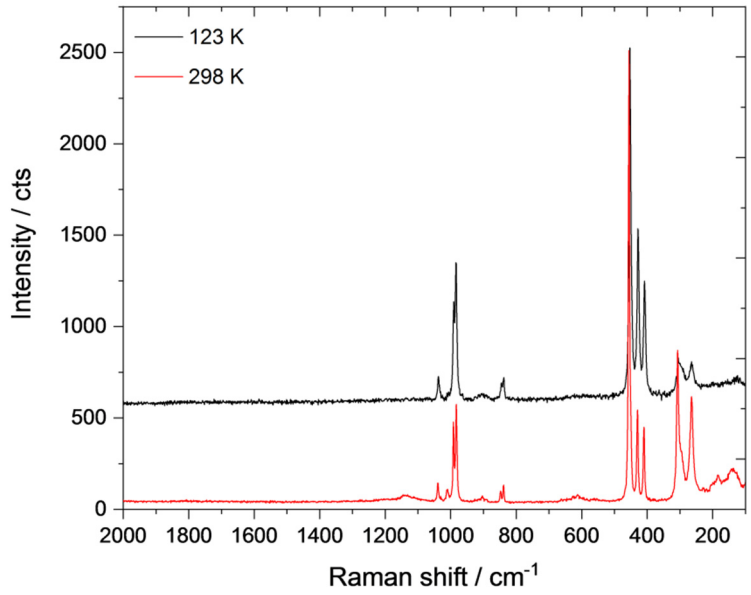



**Figure S8.** Raman spectra of the deuterated **compound 3-Mn** in the range of 1100-100 $cm^{-1}$ at 123 and 298 K.

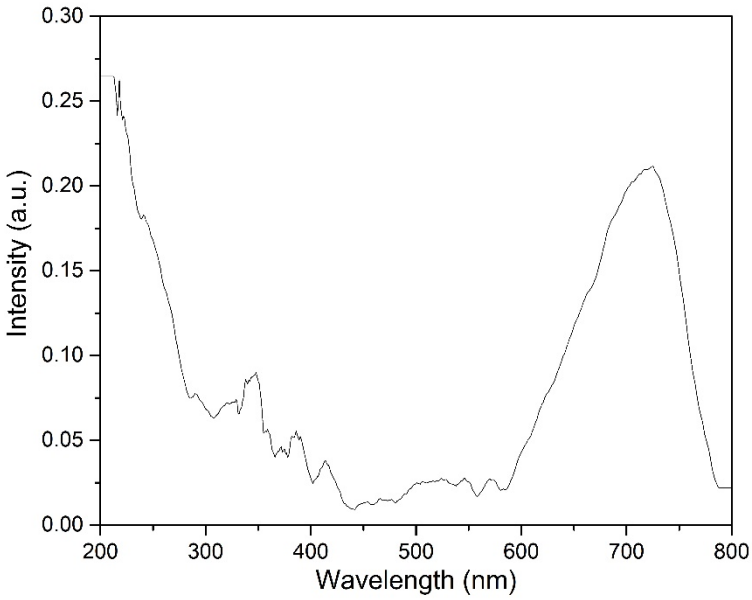
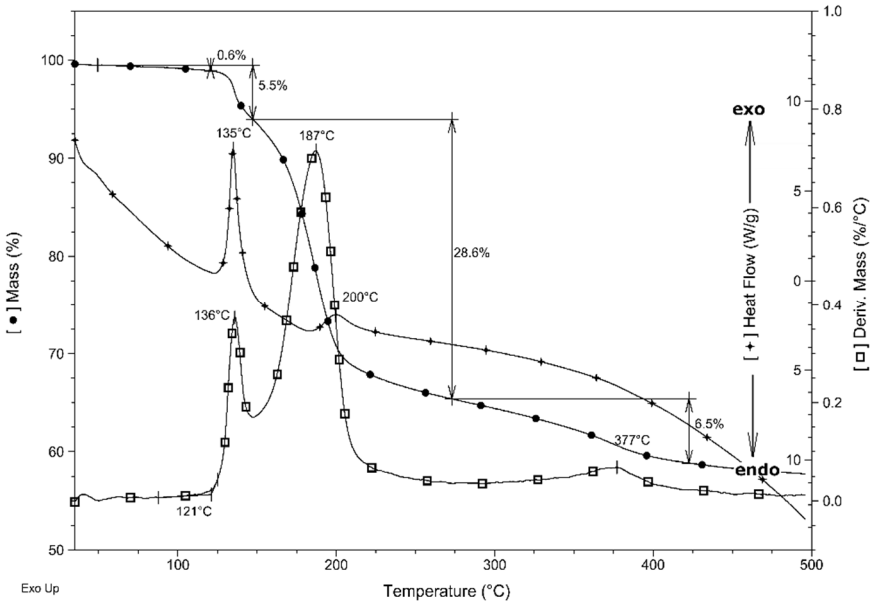



**Figure S9**. UV-VIS spectrum of **compound 3-Mn.**

(**a**)




(**b**)

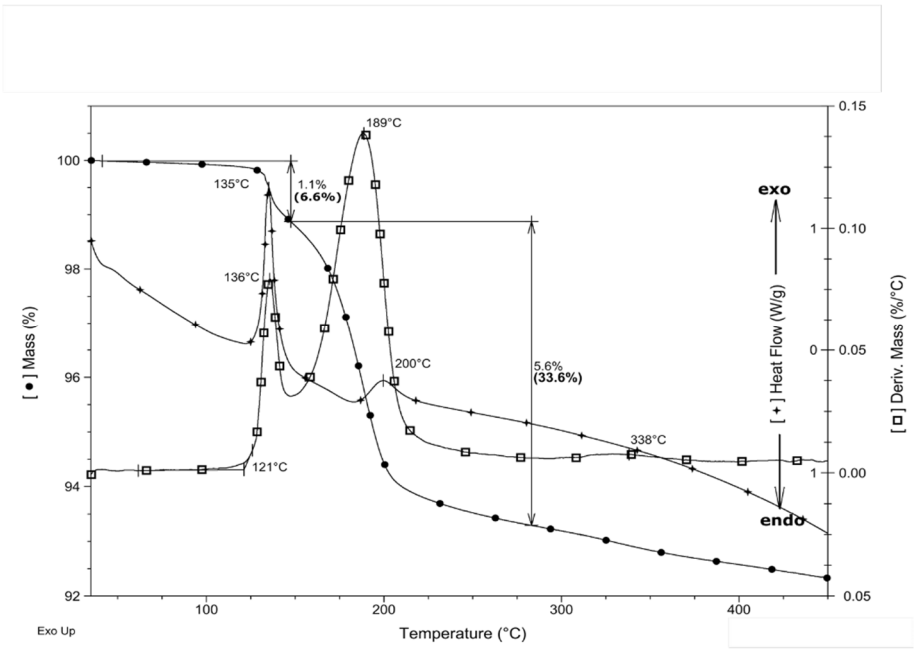
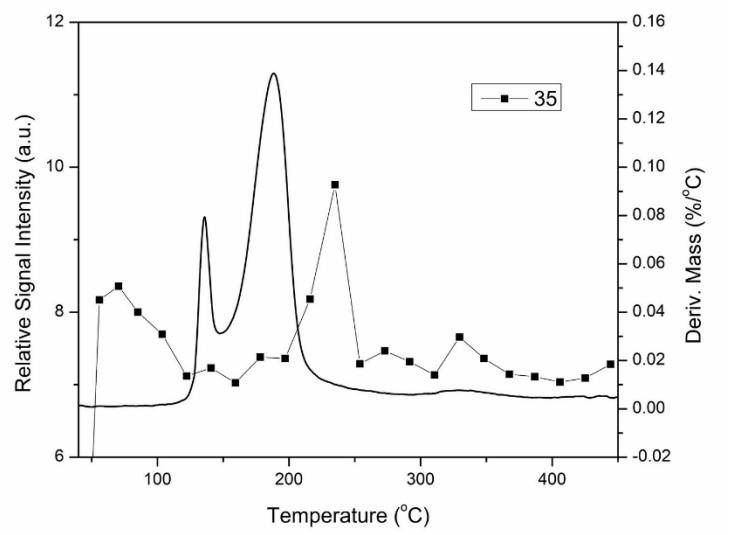
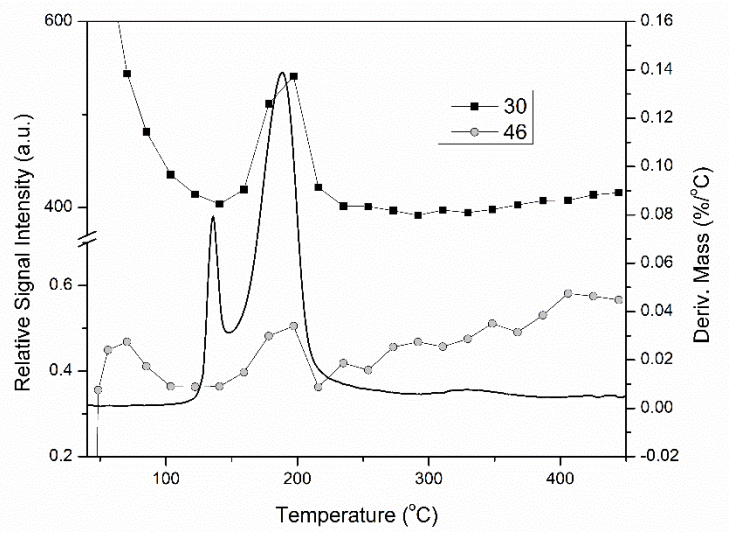
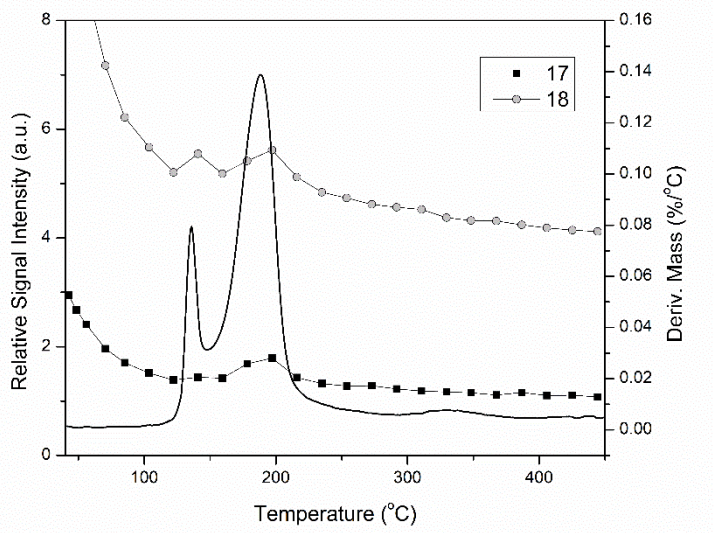



**Figure S10.** TG-DTG-DTA curves of **compound 3-Mn** in argon (**a**) and air (**b**) atmosphere.

**(a)**


35
Relative Signal Intensity (a.u.)
Deriv. Mass (%/°C)
Temperature (°C)


30
46
Relative Signal Intensity (a.u.)
Deriv. Mass (%/°C)
Temperature (°C)


17
18
Relative Signal Intensity (a.u.)
Deriv. Mass (%/°C)
Temperature (°C)

(**b**)

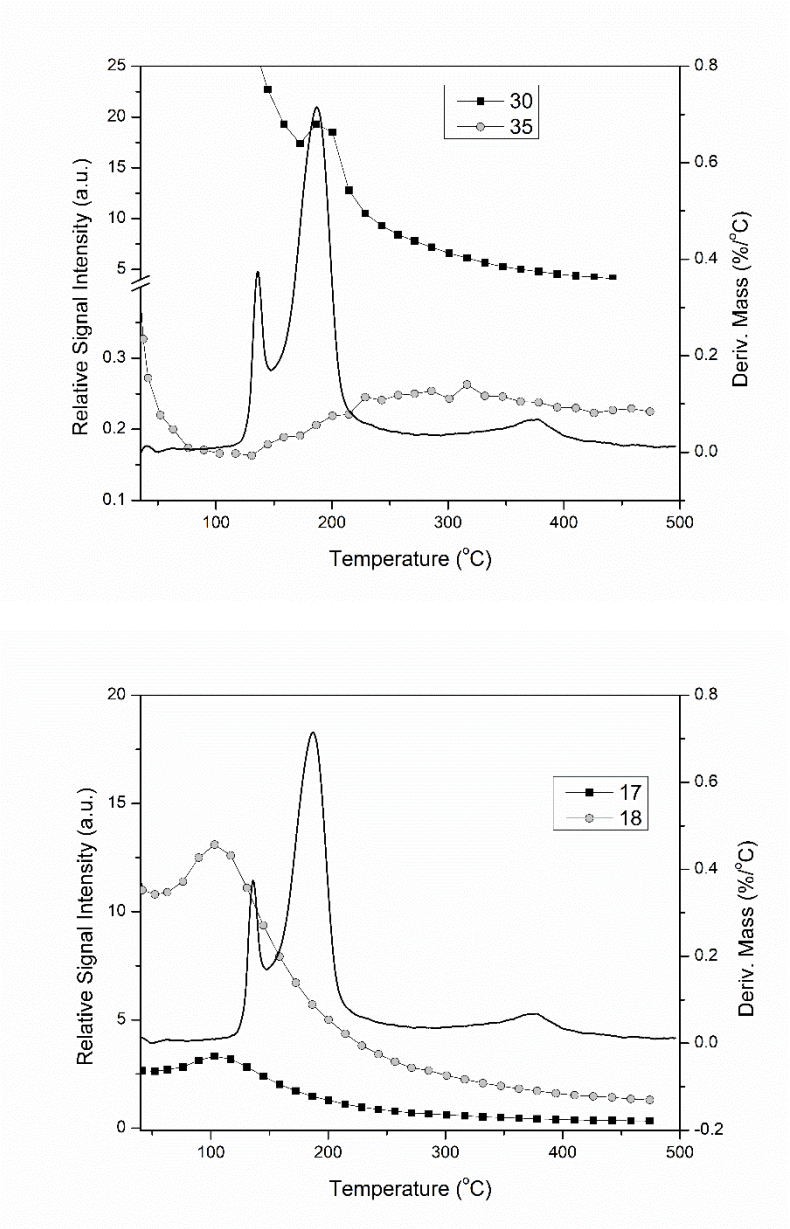
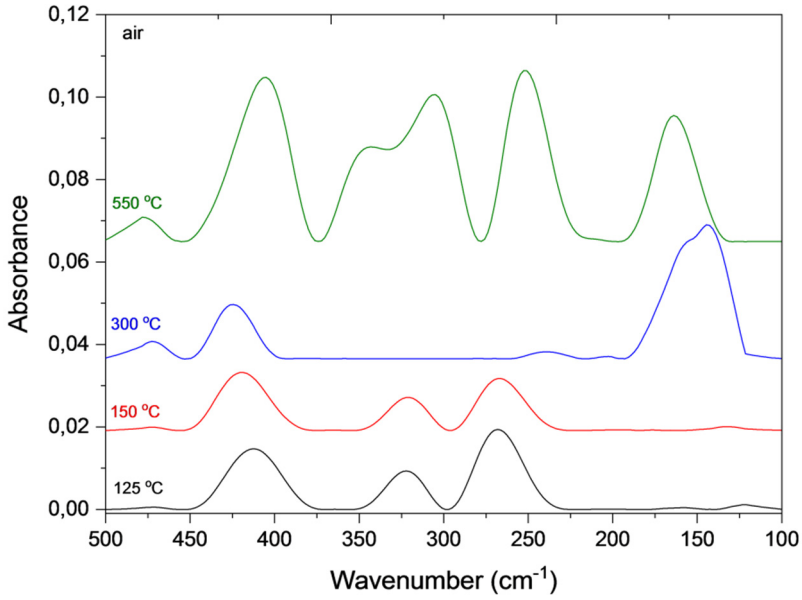



**Figure S11**. Selected TG-MS curves of **compound 3-Mn** in air (**a**) (*m*/*z* = 35, $Cl^+$; *m*/*z* = 30 ($NO^+$); *m*/*z* = 46, $NO_2^+$; *m*/*z* = 18, $H_2O^+$; *m*/*z* = 17 $OH^+$, $NH_3^+$) and argon (**b**) atmosphere (*m*/*z* = 35, $Cl^+$; *m*/*z* = 30 ($NO^+$); *m*/*z* = 18, $H_2O^+$; *m*/*z* = 17 $OH^+$, $NH_3^+$).

(**a**)




(**b**)

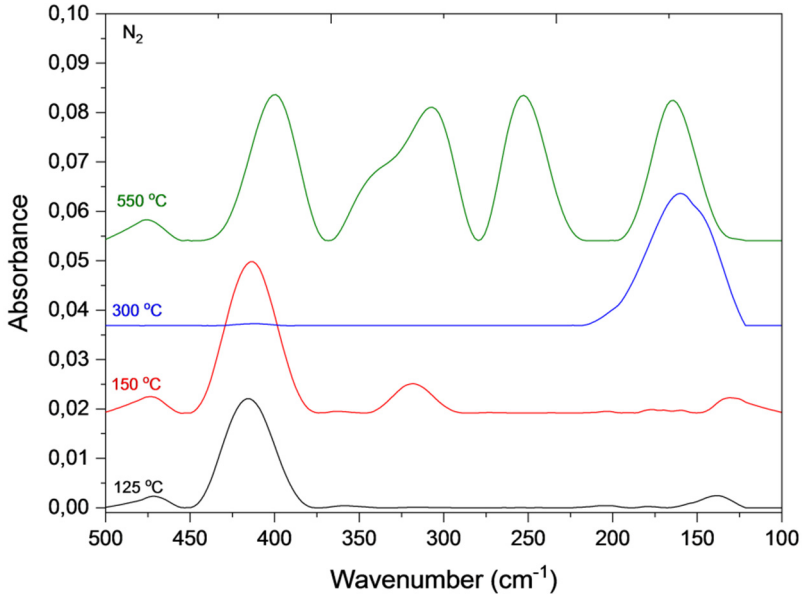
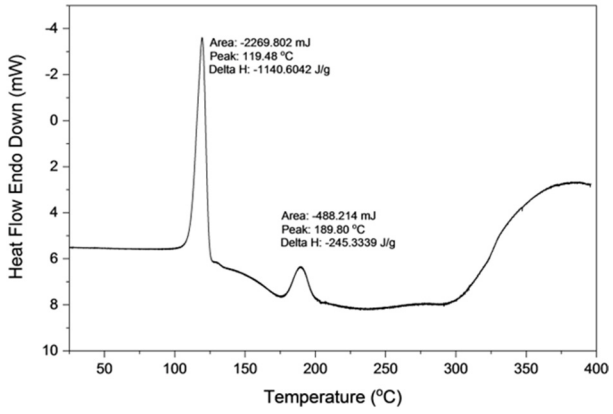



**Figure S12.** Far-IR spectra of the thermal decomposition intermediates formed from **compound 3-Mn** in air(**a**) and inert (**b**) atmosphere**.**

(**a**)




(**b**)

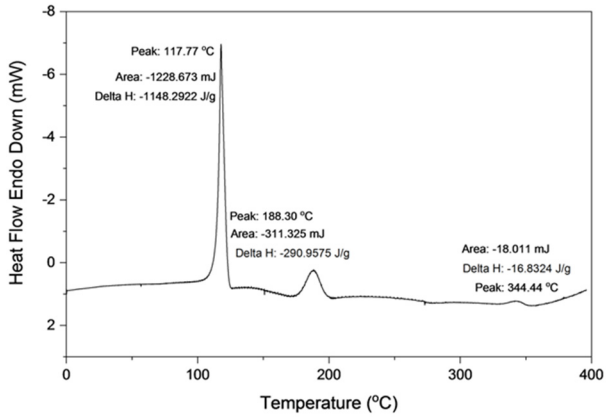



**Figure S13.** DSC analysis of **compound 3-Mn** in pure oxygen (**a**) and nitrogen (**b**).

**Table S1.** Crystal data and structure refinement of **compound 3-M.**

| | |
|---|---|
| Empirical formula | Cl Co H15 Mn2 N5 O8 |
| Formula weight | 417.43 |
| Temperature | 293(2) |
| Radiation and wavelength | Mo-Kα, λ =0.71073Å |
| Crystal system | orthorhombic |
| Space group | *C*mc2$_1$ |
| Unit cell dimensions | *a* =14.2753(7)Å<br>*b* =14.2816(6)Å<br>*c* =12.2342(5)Å<br>α =90°<br>β =90°<br>γ =90° |
| Volume | 2494.24(19)Å$^3$ |
| *Z* | 8 |
| Density (calculated) | 2.216 Mg/m$^3$ |
| Absorption coefficient, μ | 3.558 mm$^{-1}$ |
| *F*(000) | 1653 |
| Crystal colour | clear dark violet |
| Crystal description | needle |
| Crystal size | 0.5 x 0.1 x 0.05 mm |
| Absorption correction | multi-scan |
| Max. transmission | 0.53659 |
| Min. transmission | 1.00000 |
| θ–range for data collection | 3.303 ≤ θ ≤ 33.201° |
| Index ranges | -20 ≤ *h* ≤21;-21≤ *k* ≤21;-18 ≤ *l* ≤17 |
| Reflections collected | 24215 |
| Completeness to 2θ | 0.997 |
| Independent reflections | 4623 [*R*(int) =0.0571] |
| Reflections *I*>2σ(*I*) | 3848 |
| Refinement method | full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4623 /1 /173 |
| Goodness-of-fit on *F*2 | 1.067 |
| Final *R* indices [*I*>2σ(*I*)] | *R*1 =0.0395, *wR*2 =0.0746 |
| R indices (all data) | *R*1 =0.0567, *wR*2 =0.0867 |
| Max. and mean shift/esd | 0.000;0.000 |
| Largest diff. peak and hole | 0.744;-0.743 e.Å$^{-3}$ |

**Table S2.** Bond lengths (Å) and angles (°) in **compound 3-Mn.**

| | | | |
|---|---|---|---|
| Co1-N2 | 1.955(6) | Co1-N3#1 | 1.964(4) |
| Co1-N3 | 1.964(4) | Co1-N1 | 1.965(4) |
| Co1-N1#1 | 1.965(4) | Co1-Cl1 | 2.258(2) |
| Co2-N6 | 1.950(4) | Co2-N6#1 | 1.950(4) |
| Co2-N4 | 1.957(5) | Co2-N5 | 1.960(6) |
| Co2-N7 | 1.964(6) | Co2-Cl2 | 2.255(2) |
| Mn1-O3 | 1.597(4) | Mn1-O1 | 1.601(5) |
| Mn1-O4 | 1.602(5) | Mn1-O2 | 1.604(5) |
| Mn2-O7 | 1.582(5) | Mn2-O5 | 1.589(5) |
| Mn2-O6 | 1.590(6) | Mn2-O8 | 1.595(5) |

| | | | |
|---|---|---|---|
| N2-Co1-N3#1 | 89.0(2) | N2-Co1-N3 | 89.0(2) |
| N3#1-Co1-N3 | 90.7(3) | N2-Co1-N1 | 92.7(2) |
| N3#1-Co1-N1 | 89.7(2) | N3-Co1-N1 | 178.2(2) |
| N2-Co1-N1#1 | 92.7(2) | N3#1-Co1-N1#1 | 178.2(2) |
| N3-Co1-N1#1 | 89.7(2) | N1-Co1-N1#1 | 90.0(3) |
| N2-Co1-Cl1 | 179.4(2) | N3#1-Co1-Cl1 | 90.5(1) |
| N3-Co1-Cl1 | 90.5(1) | N1-Co1-Cl1 | 87.7(1) |
| N1#1-Co1-Cl1 | 87.7(1) | N6-Co2-N6#1 | 179.6(3) |
| N6-Co2-N4 | 90.0(2) | N6#1-Co2-N4 | 90.0(2) |
| N6-Co2-N5 | 90.2(2) | N6#1-Co2-N5 | 90.2(2) |
| N4-Co2-N5 | 92.1(3) | N6-Co2-N7 | 90.0(2) |
| N6#1-Co2-N7 | 90.0(2) | N4-Co2-N7 | 178.6(3) |
| N5-Co2-N7 | 89.3(3) | N6-Co2-Cl2 | 89.8(2) |
| N6#1-Co2-Cl2 | 89.8(2) | N4-Co2-Cl2 | 88.9(2) |
| N5-Co2-Cl2 | 179.0(2) | N7-Co2-Cl2 | 89.7(2) |
| O3-Mn1-O1 | 109.9(3) | O3-Mn1-O4 | 110.5(3) |
| O1-Mn1-O4 | 109.9(3) | O3-Mn1-O2 | 108.2(3) |
| O1-Mn1-O2 | 109.3(3) | O4-Mn1-O2 | 109.0(3) |
| O7-Mn2-O5 | 109.8(4) | O7-Mn2-O6 | 110.2(4) |
| O5-Mn2-O6 | 107.0(3) | O7-Mn2-O8 | 111.2(3) |
| O5-Mn2-O8 | 112.0(4) | O6-Mn2-O8 | 106.7(3) |

Symmetry codes to generate equivalent atoms: 1. [4_655] -x+1,y,z.

**Table S3.** Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg in the crystal of $[Co(NH_3)_5Cl](MnO_4)_2$ (distances are given in Å).

| Nr | Typ Res | Donor | --- H | ....Acceptor | Symm. op. | D - H | H...A | D...A | D - H...A |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | N1 | --H1A | ..Cl2 | x,y,-1+z | 0.89 | 2.74 | 3.603(5) | 164° |
| 3 | 1 | N1 | --H1B | ..O2 | 1/2+x,1/2-y,1/2+z | 0.89 | 2.23 | 3.104(6) | 165° |
| 4 | 1 | N1 | --H1C | ..O8 | x,y,z | 0.89 | 2.05 | 2.932(8) | 169° |
| 5 | 1 | N2 | --H2A | ..Cl1 | 1-x,1-y,1/2+z | 0.89 | 2.53 | 3.361(6) | 156° |
| 7 | 1 | N2 | --H2B | ..O8 | 1-x,y,z | 0.89 | 2.05 | 2.894(7) | 158° |
| 8 | 1 | N2 | --H2C | ..O8 | x,y,z | 0.89 | 2.10 | 2.894(7) | 148° |
| 9 | 1 | N3 | --H3A | ..Cl2 | 1-x,1-y,-1/2+z | 0.89 | 2.64 | 3.512(5) | 165° |
| 11 | 1 | N3 | --H3B | ..O2 | 1/2+x,1/2+y,z | 0.89 | 2.27 | 3.065(6) | 148° |
| 12 | 1 | N3 | --H3B | ..O3 | 1/2+x,1/2+y,z | 0.89 | 2.46 | 3.234(6) | 145° |
| 13 | 1 | N3 | --H3C | ..O1 | 1/2-x,1/2+y,z | 0.89 | 2.14 | 3.024(7) | 173° |
| 14 | 2 | N4 | --H4A | ..O3 | 1/2-x,1/2-y,1/2+z | 0.89 | 2.33 | 3.046(5) | 138° |
| 15 | 2 | N4 | --H4B | ..O7 | x,y,z | 0.89 | 2.02 | 2.860(8) | 157° |
| 16 | 2 | N4 | --H4B | ..O7 | 1-x,y,z | 0.89 | 2.47 | 2.860(8) | 107° |
| 17 | 2 | N4 | --H4C | ..O7 | 1-x,y,z | 0.89 | 2.56 | 2.860(8) | 101° |
| 18 | 2 | N4 | --H4C | ..O3 | 1/2-x,1/2+y,z | 0.89 | 2.18 | 3.046(5) | 163° |
| 19 | 2 | N5 | --H5A | ..O7 | 1-x,y,z | 0.89 | 2.19 | 3.022(8) | 156° |
| 20 | 2 | N5 | --H5B | ..O5 | 1-x,-y,1/2+z | 0.89 | 2.63 | 3.226(8) | 125° |
| 21 | 2 | N5 | --H5C | ..O5 | 1-x,-y,1/2+z | 0.89 | 2.42 | 3.226(8) | 151° |
| 22 | Intra 2 | N6 | --H6A | ..Cl2 |  | 0.89 | 2.65 | 2.975(5) | 103° |
| 23 | 2 | N6 | --H6B | ..O1 | x,y,1+z | 0.89 | 2.47 | 3.079(8) | 126° |
| 24 | 2 | N6 | --H6B | ..O5 | x,-y,1/2+z | 0.89 | 2.18 | 3.007(7) | 153° |
| 25 | 2 | N6 | --H6C | ..O3 | 1/2-x,1/2-y,1/2+z | 0.89 | 2.56 | 3.005(7) | 111° |
| 26 | 2 | N7 | --H7A | ..O5 | 1-x,-y,1/2+z | 0.89 | 2.44 | 3.017(8) | 123° |
| 27 | 2 | N7 | --H7A | ..O4 | 1-x,y,1+z | 0.89 | 2.35 | 2.960(8) | 126° |
| 28 | 2 | N7 | --H7B | ..O5 | x,-y,1/2+z | 0.89 | 2.24 | 3.017(8) | 145° |
| 29 | 2 | N7 | --H7C | ..O4 | x,y,1+z | 0.89 | 2.10 | 2.960(8) | 161° |

## *References*

[1] *CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.*

[2] *G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.*

[3] *O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341.*