Supplementary Materials: Structural and Gas Retention Changes Induced by Ozonization of Cobalt(II) and Manganese(II) Hexacyanocobaltates(III)

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1. FTIR Spectra of Samples

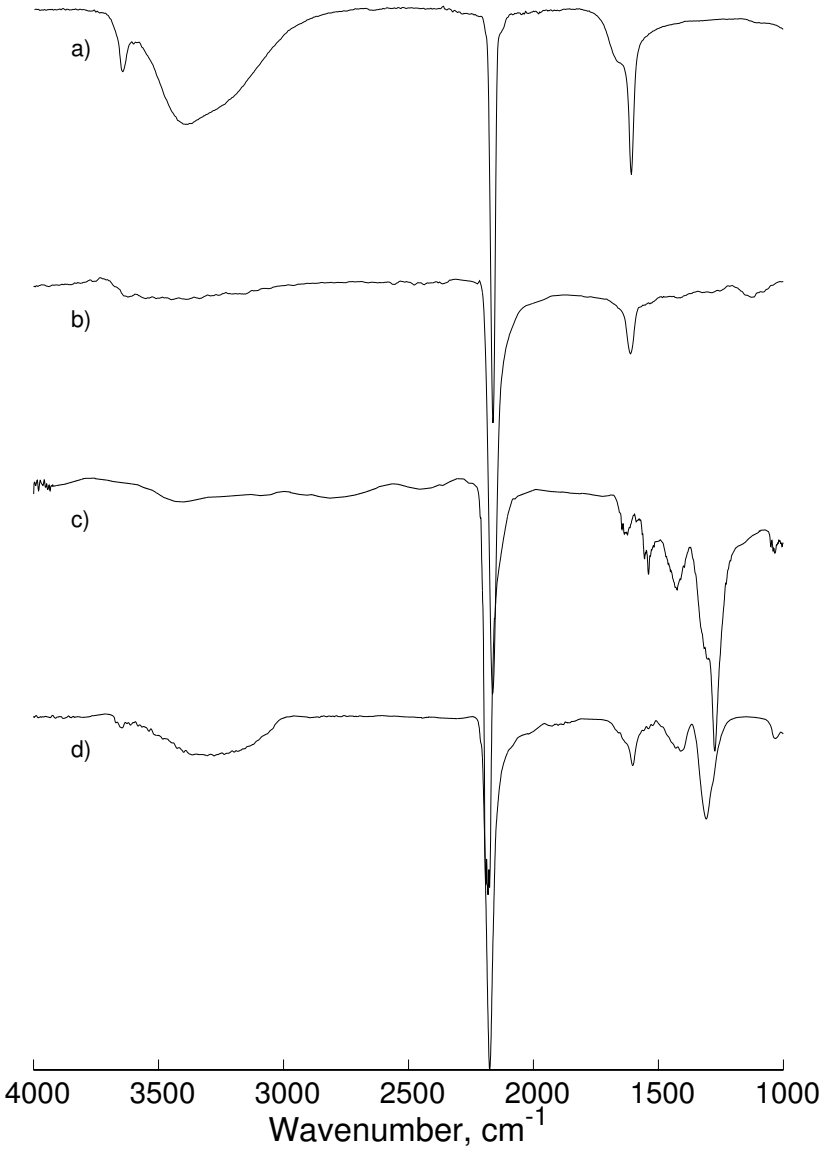

Figure S1. Full FTIR spectra of MnHCC: (**a**) as synthesized; (**b**) partially dehydrated; (**c**) ozonized and partially dehydrated; (**d**) ozonized and hydrated.

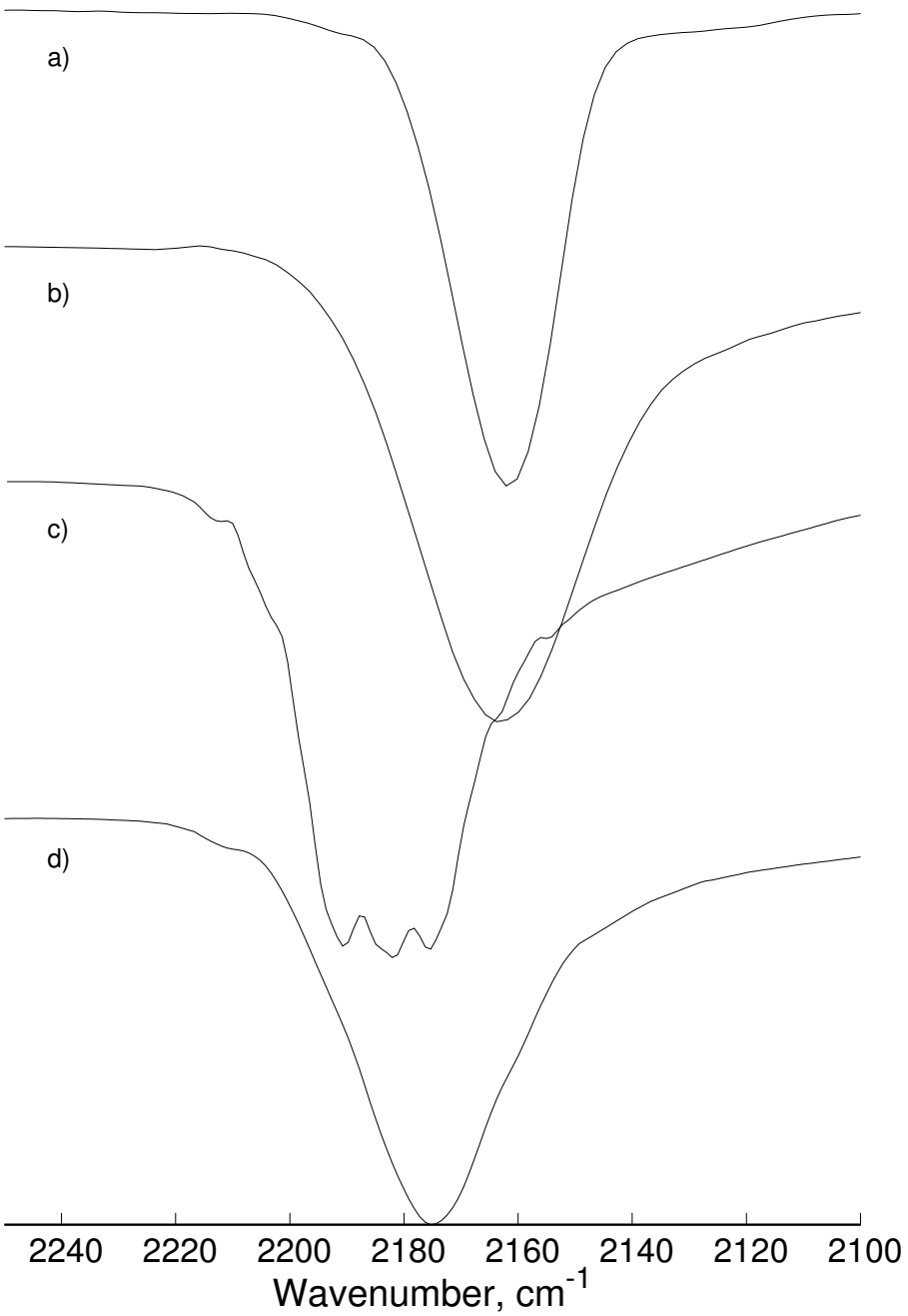

Figure S2. Section of ν(CN) bands of MnHCC FTIR spectra: (**a**) as synthesized; (**b**) partially dehydrated; (**c**) ozonized and partially dehydrated; (**d**) ozonized and hydrated.

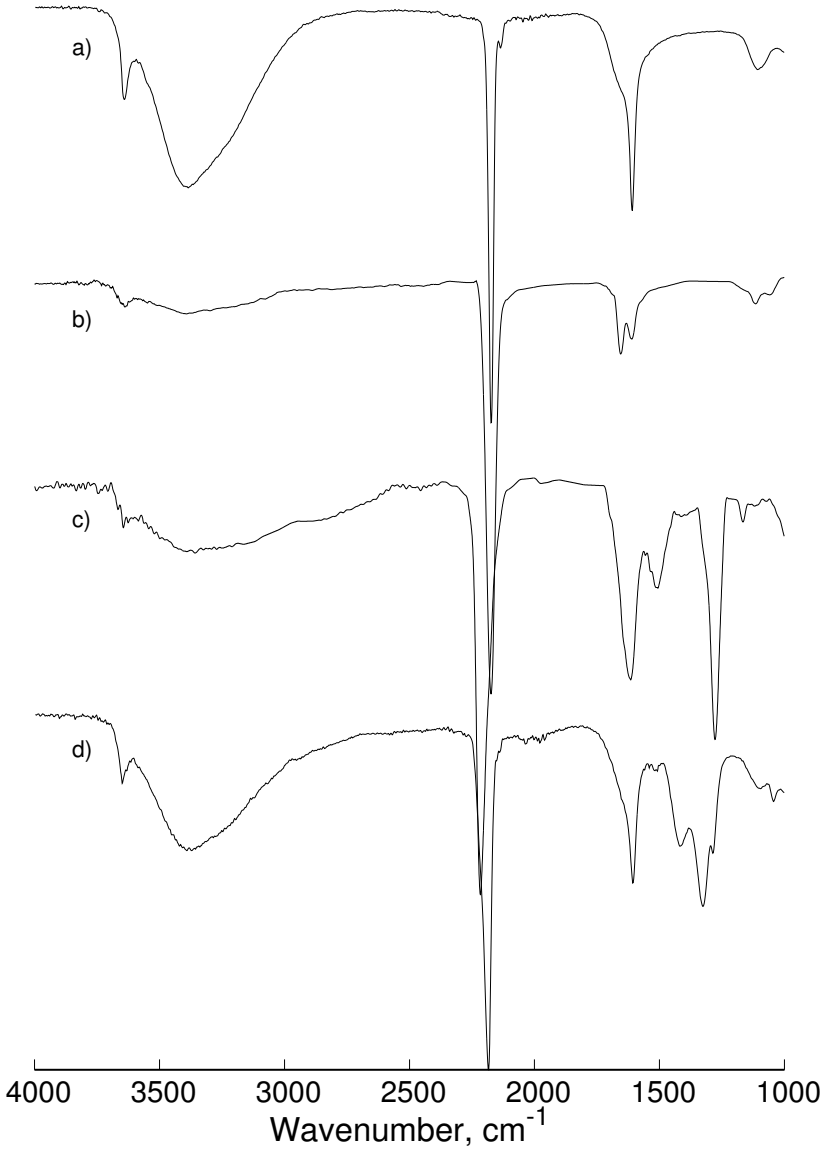

Figure S3. Full FTIR spectra of CoHCC: (**a**) as synthesized; (**b**) partially dehydrated; (**c**) ozonized and partially dehydrated; (**d**) ozonized and hydrated.

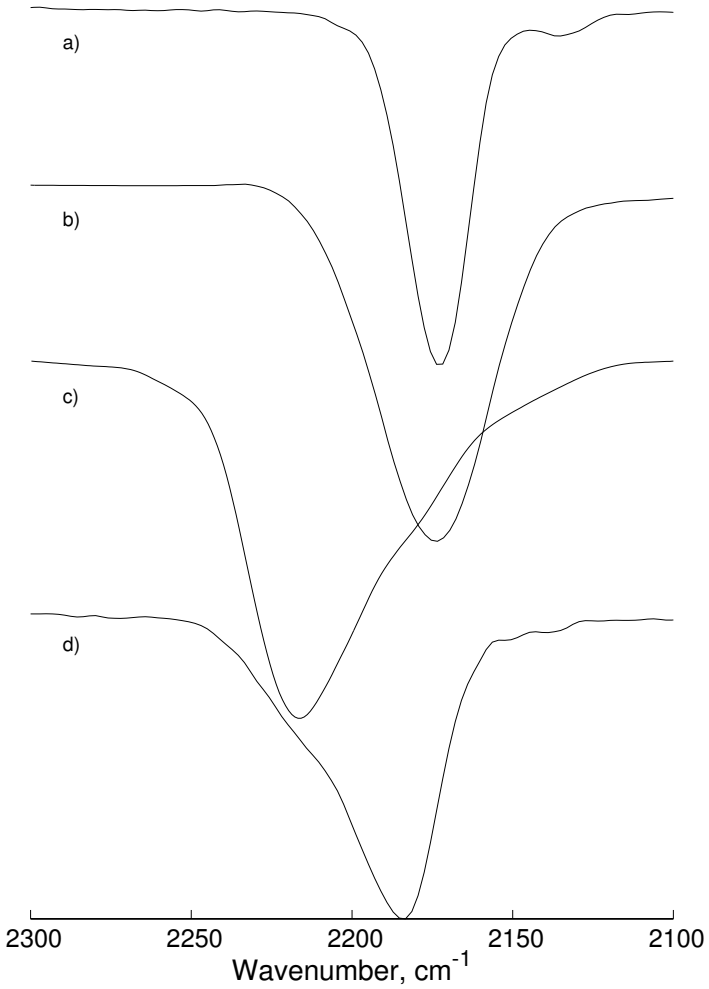

Figure S4. Section of ν(CN) bands of CoHCC FTIR spectra: (**a**) as synthesized; (**b**) partially dehydrated; (**c**) ozonized and partially dehydrated; (**d**) ozonized and hydrated.

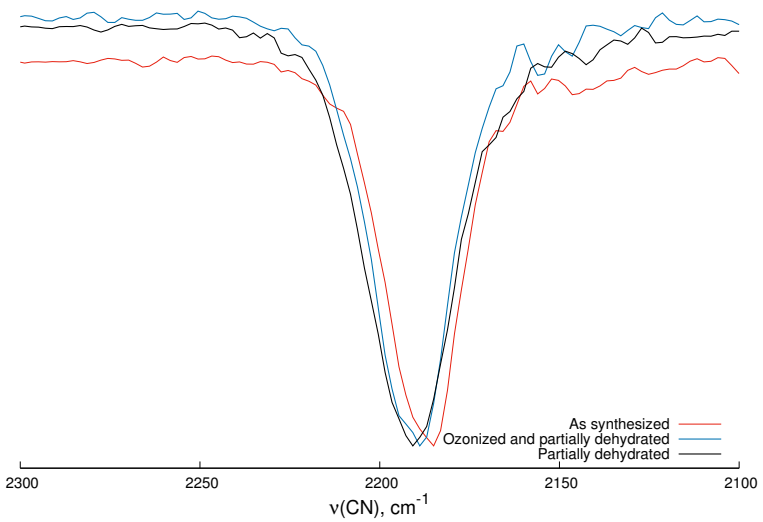

Figure S5. Section of ν(CN) bands of CuHCC FTIR spectra.

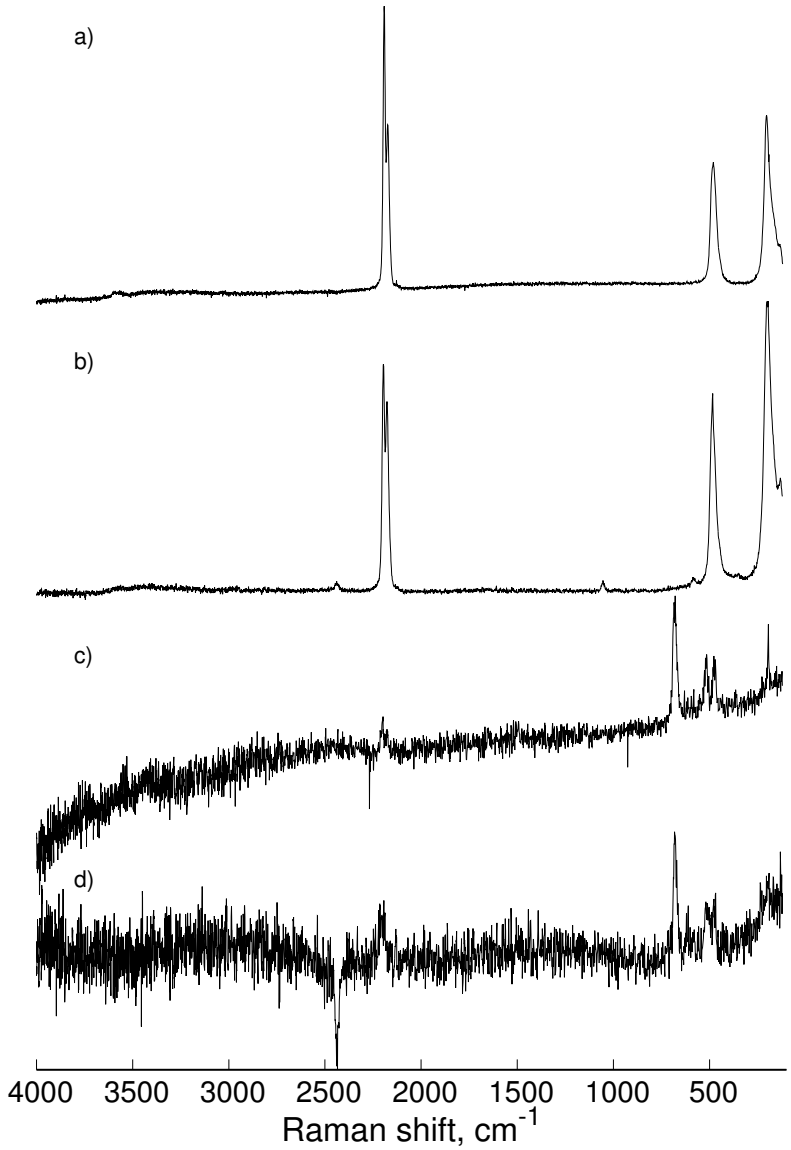

Figure S6. Full Raman spectra of: (**a**) MnHCC as synthesized; (**b**) MnHCCOz saturated with methanol and then saturated in water vapor; (**c**) CoHCC as synthesized; (**d**) CoHCCOz saturated with methanol and then saturated in water vapor.

2. X-ray Diffraction Powder Patterns of Samples

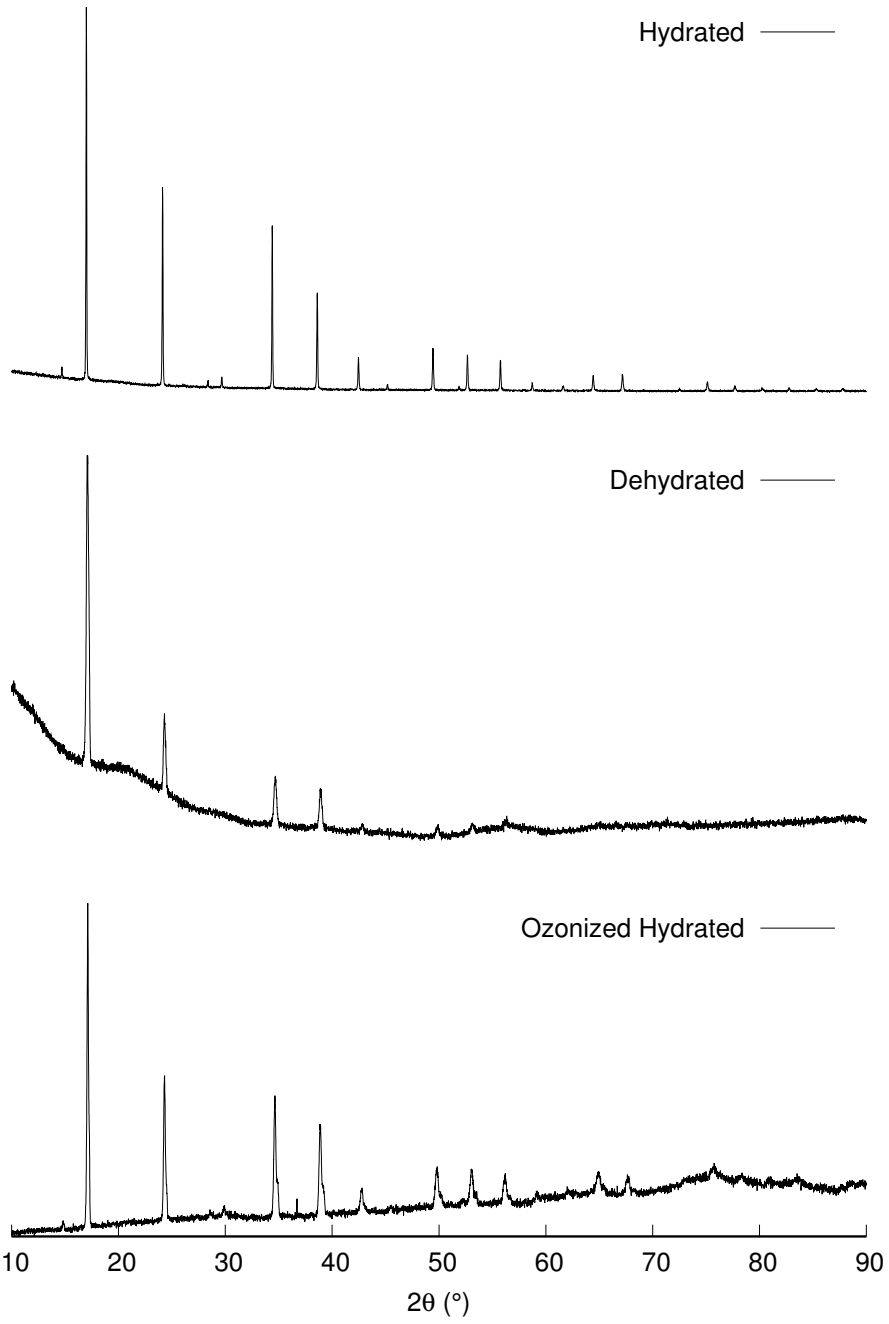

Figure S7. X-ray diffraction powder patterns of MnHCC.

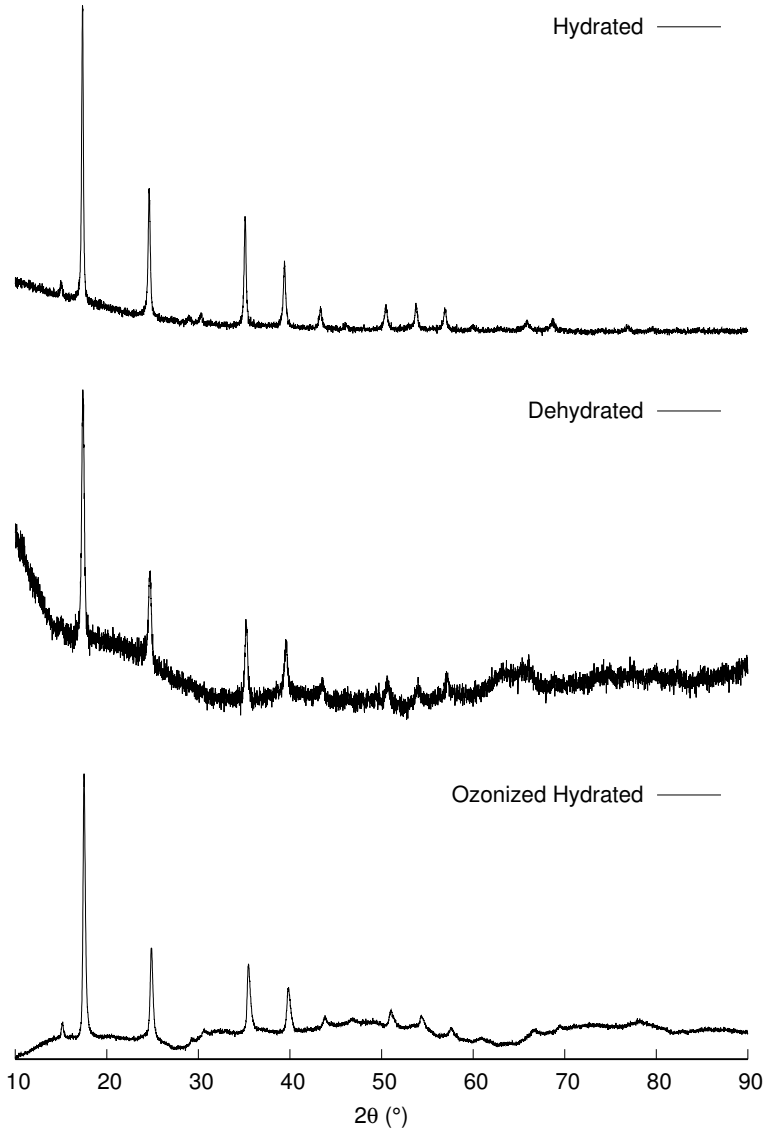

Figure S8. X-ray diffraction powder patterns of CoHCC.

3. Hydrogen Adsorption

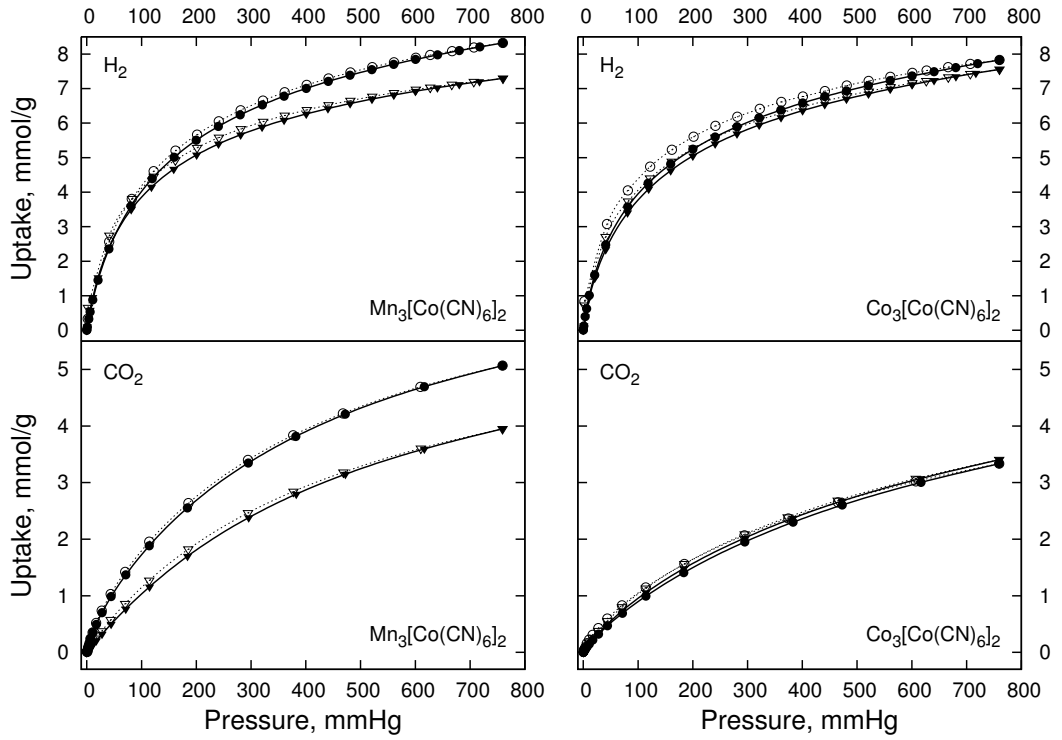

Figure S9. Hydrogen adsorption isotherms at 77 K and carbon dioxide adsorption isotherms at 273.15 K of the degasified samples. Adsorption branch is plotted with filled symbols and desorption branch by open symbols. The isotherms on the unmodified samples is represented with circles and the isotherms of ozonized samples are represented by triangles. Lines are cubic spline of experimental data to guide the reader.

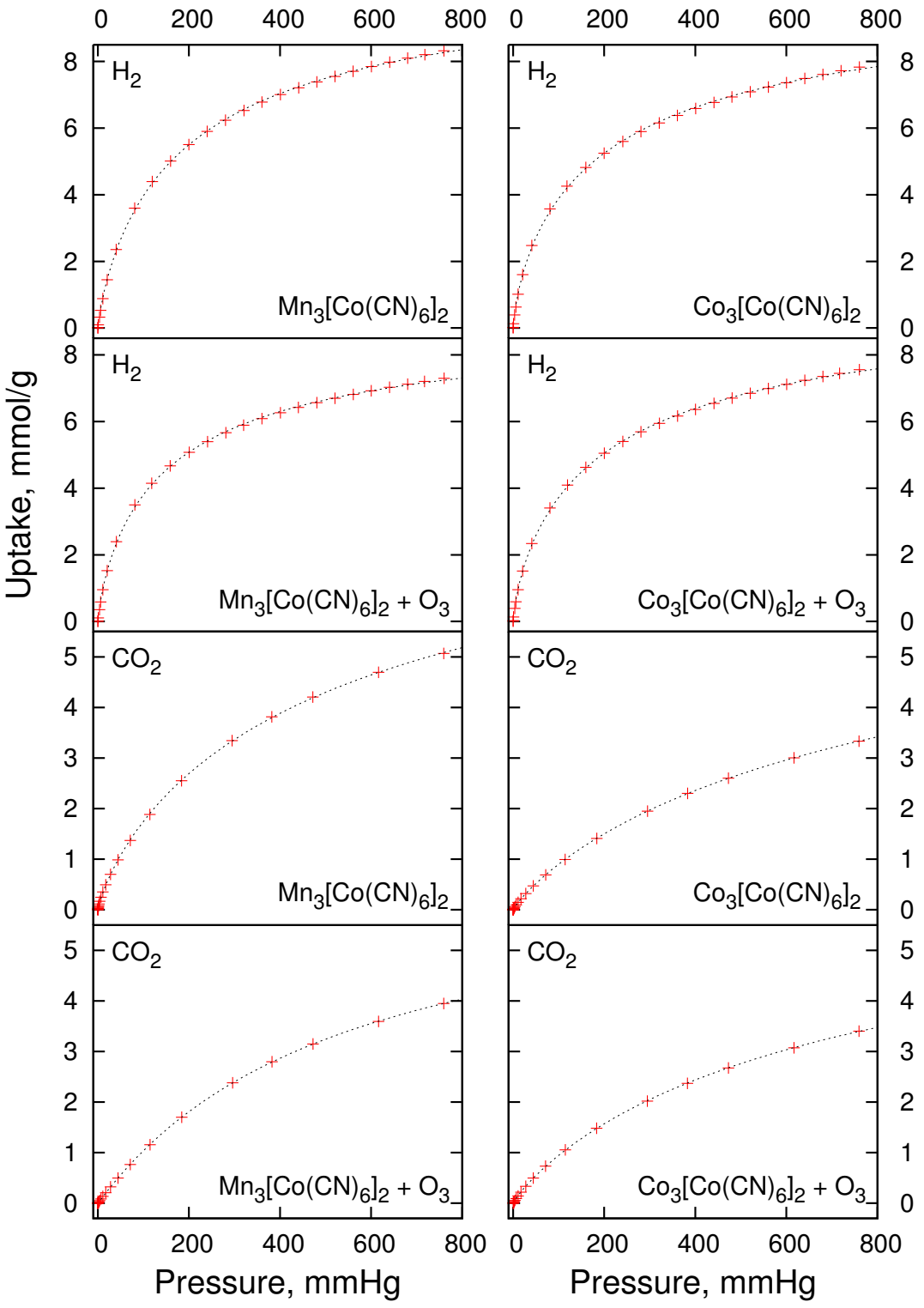

Figure S10. Langmuir-Freundlich isotherm fit (dashed line) to experimental isotherms (red crosses).

4. Thermogravimetric Analysis

Hydrated trimanganese bis(hexakis(cyano)cobaltate) and tricobaltate bis(hexakis(cyano)cobaltate) have 6 coordinated water molecules [1]. The number of uncoordinated water molecules changes with the environmental conditions the samples are submitted to. So, the molecular formula for each compound is:

$$M_3(H_2O)_6[Co(CN)_6]_2 \cdot nH_2O \qquad M = Mn, Co.$$

Thermal evolution is described by three events in each case.

For M=Mn

Reaction of the thermal event	Description
$Mn_3(H_2O)_6[Co(CN)_6]_2{\cdot}nH_2O \xrightarrow{Q} Mn_3(H_2O)_6[Co(CN)_6]_2 + nH_2O\uparrow$	Uncoord. H_2O
$Mn_3(H_2O)_6[Co(CN)_6]_2 \xrightarrow{Q} Mn_3[Co(CN)_6]_2 + 6\,H_2O\uparrow$	Coord. H_2O
$Mn_3[Co(CN)_6]_2 + \frac{15}{4}\,O_2(g) \xrightarrow{Q} \frac{1}{2}\,\alpha{-}Mn_2O_3 + 2\,CoMnO_3 + 6\,C_2N_2\uparrow$	Decomposition

The Co–Mn phase diagram at 400 °C and $Co/(Co + Mn) = 0.4$, suggest the formation of $\alpha{-}Mn_2O_3$ and the intermetalic $CoMnO_3$ ([2], Figure 1).

Global reaction is:

$$Mn_3(H_2O)_6[Co(CN)_6]_2{\cdot}nH_2O + \tfrac{15}{4}\,O_2(g) \xrightarrow{Q} nH_2O\uparrow + 6\,H_2O\uparrow + \tfrac{1}{2}\,Mn_2O_3 + \\ + 2\,CoMnO_3 + 6\,C_2N_2\uparrow$$

For M=Co

Reaction of the thermal event	Description
$Co_3(H_2O)_6[Co(CN)_6]_2 \cdot nH_2O \xrightarrow{Q} Co_3(H_2O)_6[Co(CN)_6]_2 + nH_2O\uparrow$	Uncoord. H_2O
$Co_3(H_2O)_6[Co(CN)_6]_2 \xrightarrow{Q} Co_3[Co(CN)_6]_2 + 6\,H_2O\uparrow$	Coord. H_2O
$Co_3[Co(CN)_6]_2 + \frac{10}{3}\,O_2(g) \xrightarrow{Q} \frac{5}{3}\,Co_3O_4 + 6\,C_2N_2\uparrow$	Decomposition

Global reaction:

$$Co_3(H_2O)_6[Co(CN)_6]_2{\cdot}nH_2O + \tfrac{10}{3}\,O_2(g) \xrightarrow{Q} nH_2O\uparrow + 6\,H_2O\uparrow + \tfrac{5}{3}\,Co_3O_4 + \\ + 6\,C_2N_2\uparrow$$

The uncoordinated and coordinated water molecules evolve in one event from room temperature to 346.26 °C for MnHCC with a weight loss of 27.47 % (Figure S11) and from room temperature to 313.10 °C for CoHCC, with a weight loss of 29.48 % (Figure S12). Solving for uncoordinated number of water molecules (Table S1)

Table S1. Molar mass of decomposition reaction components.

Fomula	MW, g/mol
$Co_3(H_2O)_6[Co(CN)_6]_2$	714.965
$Mn_3(H_2O)_6[Co(CN)_6]_2$	702.987
Co_3O_4	240.797
$CoMnO_3$	161.868
Mn_2O_3	157.873
C_2N_2	52.036
H_2O	18.015
O_2	31.998

$$\frac{18.015(6+n)}{702.987+18.015n} \times 100\,\% = 27.47\,\%$$

$n = 6.51$ uncoordinated H_2O molecules for MnHCC

$$\frac{18.015(6+n)}{714.965+18.015n} \times 100\,\% = 29.48\,\%$$

$n = 8.08$ uncoordinated H_2O molecules for CoHCC

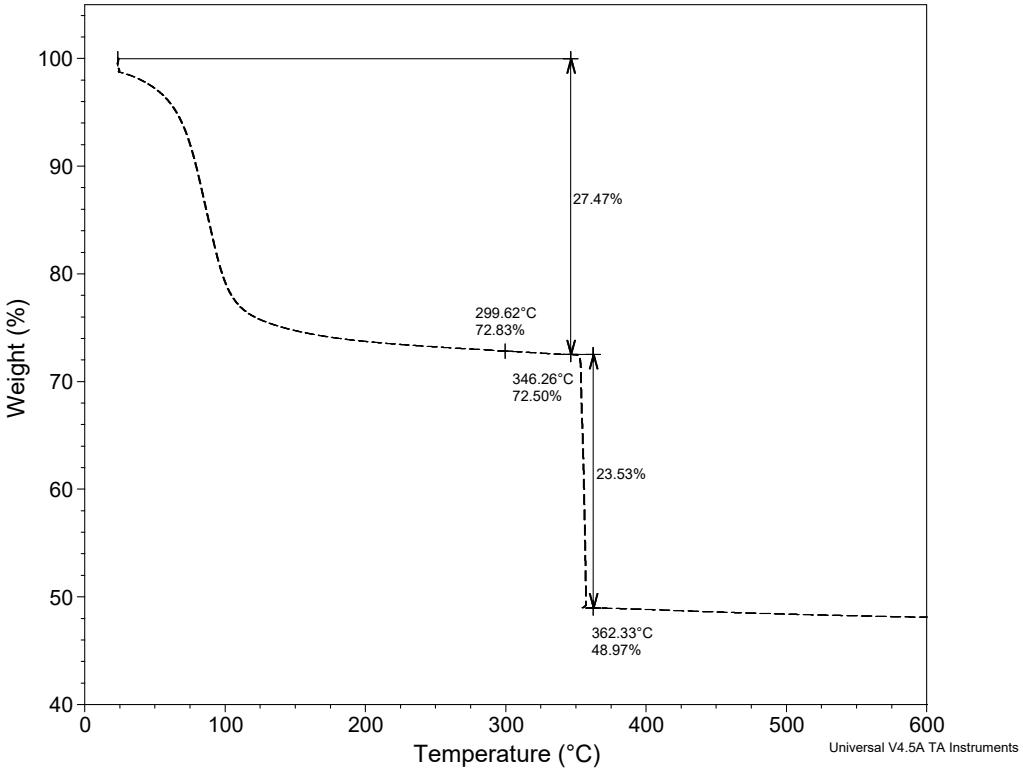

Figure S11. Thermogravimetric experimental curve for MnHCC as synthesized.

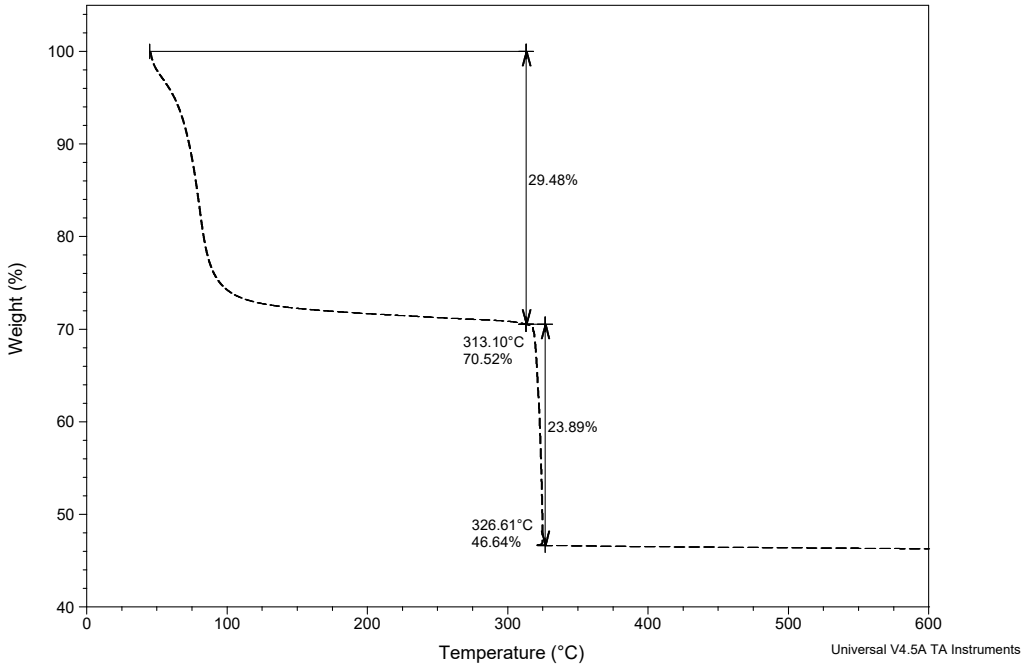

Figure S12. Thermogravimetric experimental curve for CoHCC as synthesized.

Substituting n in $M_3(H_2O)_6[Co(CN)_6]_2 \cdot nH_2O$ and estimating the weight percent of the residue in each case:

For M = Mn

$$\frac{\frac{1}{2}157.873 + 2 \times 161.868}{702.987 + 6.51 \times 18.015} \times 100\% = 49.09\%$$

The observed value at 362.33 °C was 48.97% (Figure S11) with a deviation of 0.24%.

For M = Co

$$\frac{\frac{5}{3}240.797}{714.965 + 8.082 \times 18.015} \times 100\% = 46.64\%$$

The observed value at 326.61 °C was 46.64% (Figure S12) in agreement with our result.

To estimate the weight loss due to C_2N_2 corresponding to the decomposition event, O_2 weight gain should be taking into account.

For M = Mn

$$\frac{6 \times 52.036 - \frac{15}{4}31.998}{702.987 + 6.51 \times 18.015}100\% = 23.43\%$$

The observed weight loss between 346.26 °C and 362.33 °C was 23.53% (Figure S11).

For M = Co

$$\frac{6 \times 52.036 - \frac{10}{3}31.998}{714.965 + 8.082 \times 18.015}100\% = 23.89\%$$

The observed weight loss between 313.10 °C and 326.61 °C was 23.89% (Figure S12).

The effect of the O_3 on $M_3[Co(CN)_6]_2$ is a charge transfer from M^{2+} to Co^{3+}. This charge transfer is reversed at decomposition temperature. So, while the charge transfer affect the thermal evolution of water it does not change the final products and the global reaction of thermal evolution is the same.

To analyze ozonized thermogravimetric curves, is important to consider that in these cases the thermal events corresponding to water evolution and decomposition overlaps. So, is convenient to estimate n from the residue.

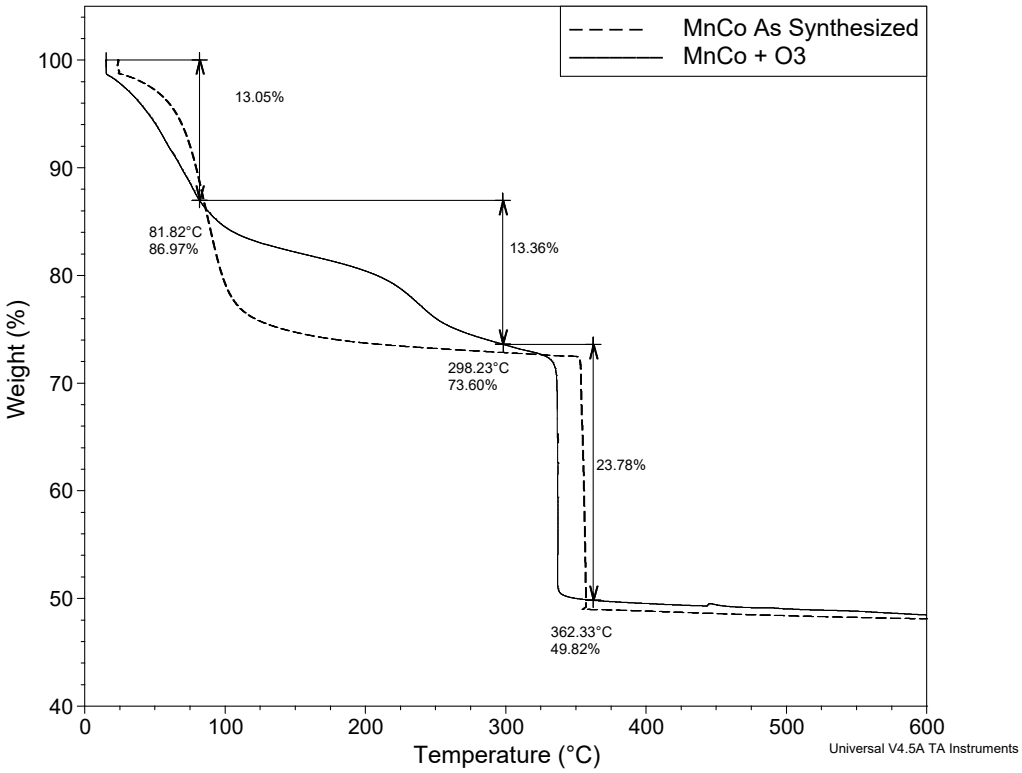

Figure S13. Thermogram of trimanganese bis(hexakis(cyano)cobaltate) as synthesized and ozonized.

For M = Mn at 362.33 °C (49.82 %) (Figure S13)

$$\frac{\frac{1}{2}157.873 + 2 \times 161.868}{702.987 + n \times 18.015} \times 100\% = 49.82\%$$

$$n = 5.84 \text{ uncoordinated } H_2O \text{ molecules}$$

For M = Co at 266.03 °C (47.46 %)

$$\frac{\frac{5}{3}240.797}{714.965 + n \times 18.015} \times 100\% = 47.46\%$$

$$n = 7.25 \text{ uncoordinated } H_2O \text{ molecules}$$

This result is consistent with the reduction of cell parameter due to ozonization. The accessible pore volume is reduced as a consequence of the cell parameter reduction. Calculating the weight loss associated to the evolution of C_2N_2 we can estimate the temperature at which the decomposition starts.

For M = Mn

$$\frac{6 \times 52.036 - \frac{15}{4}31.998}{702.987 + 5.84 \times 18.015}100\% = 23.78\%$$

The decomposition process starts at 298.23 °C according to Figure S13. The weight loss due to the coordinate water molecules evolution in ozonized sample is:

$$\frac{6 \times 18.015}{702.987 + 5.84 \times 18.015} \times 100\% = 13.37\%$$

According to this value, the evolution of coordinated water molecules start at 81.82 °C (Figure S13).

For M = Co

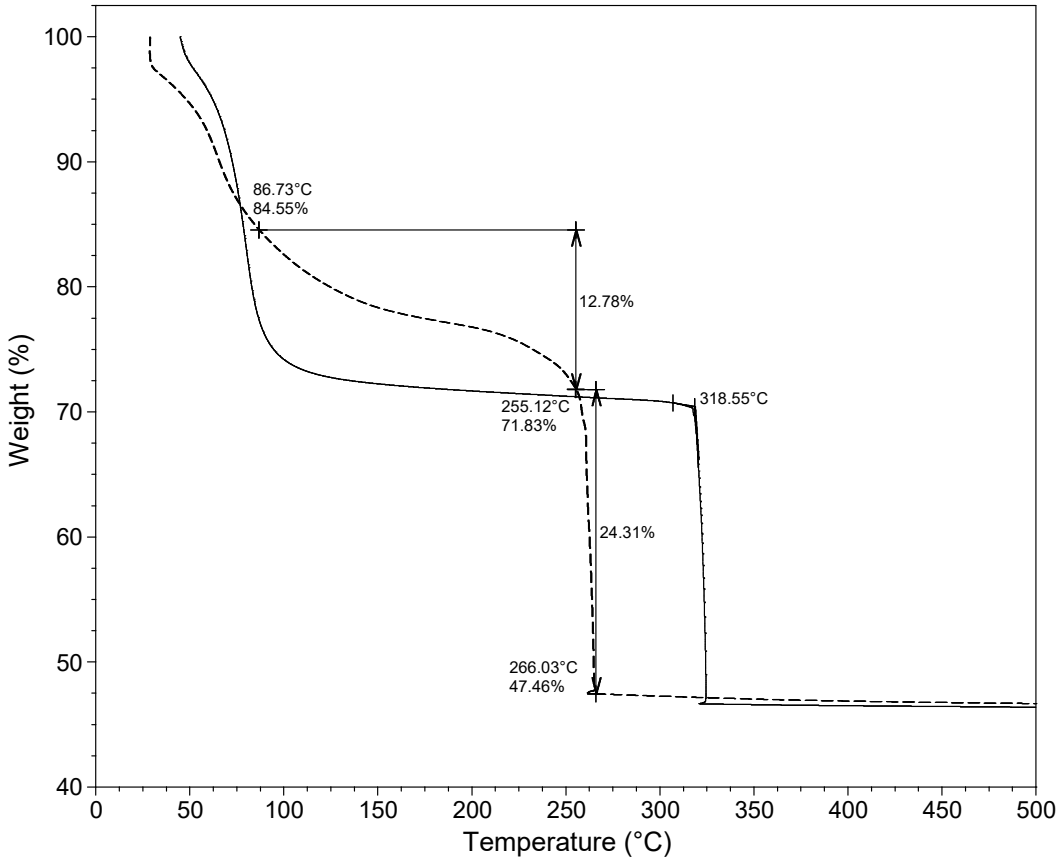

Figure S14. Thermogram of tricobalt bis(hexakis(cyano)cobaltate) as synthesized (continuous line) and ozonized (dashed line).

$$\frac{6 \times 52.036 - \frac{10}{3} 31.998}{714.965 + 7.252 \times 18.015} 100\% = 24.31\%$$

The decomposition process starts at 255.33 °C according to Figure S14 and the weight loss due to the coordinate water molecules evolution in ozonized sample is:

$$\frac{6 \times 18.015}{714.965 + 7.252 \times 18.015} \times 100\% = 12.782\%$$

According to this value, the evolution of coordinated water molecules start at 86.73 °C.

After been ozonized, both materials thermogravimetric curves exhibit similar behaviour: they weight losses due to dehydration for temperatures above 150 °C increases and decomposition processes begin at lower temperatures in comparizon with the original curves (Figures S13 and S14). Dehydration process still goes from room temperature until decomposition in both materials, at 255.33 °C for CoHCCOz with a weight loss of 28.33%, and at 298.23 °C for MnHCCOz with a corresponding weight loss of 26.40%, but with different behavior compared with original materials curves. From 150 °C until decomposition, weight losses for original materials are relative small (2.15% for MnHCC and 1.71% for CoHCC) while the corresponding weight loss in ozonized samples are 8.78% for MnHCCOz and 6.59% for CoHCCOz. This can be explained considering how the oxidation of the metallic centers affects the interaction of both types of water molecules inside the structure. Hydrogen bonds and van de Waals forces between non–coordinated water molecules

are poorly affected by the change in the local electric field around the superficial metals, but the coordination interaction is strengthened because water molecules are polar and the oxidation increases the positive charge at the metallic centers. This strengthened explains why ozonized materials curves have corresponding inflection points at 76.82 °C and 85.83 °C. The hydration degree was estimated from the residue. MnHCCOz has 5.84 uncoordinated water molecules per formula unit and CoHCCOz has 7.25. The weight losses by dehydration are smaller than the original samples ones as expected, because of the cell parameter reduction after ozonization, consistent with experimental XRD data. Decomposition event occurs from 298.23 °C to 362.33 °C for MnHCCOz and from 255.33 °C to 266.03 °C for CoHCCOz with weight losses of 23.78% and 24.31%, both associated with the loss of the CN^- groups. Decomposition begin at lower temperatures due to the structural instability caused by the change of the electronic density in ozonized structures.

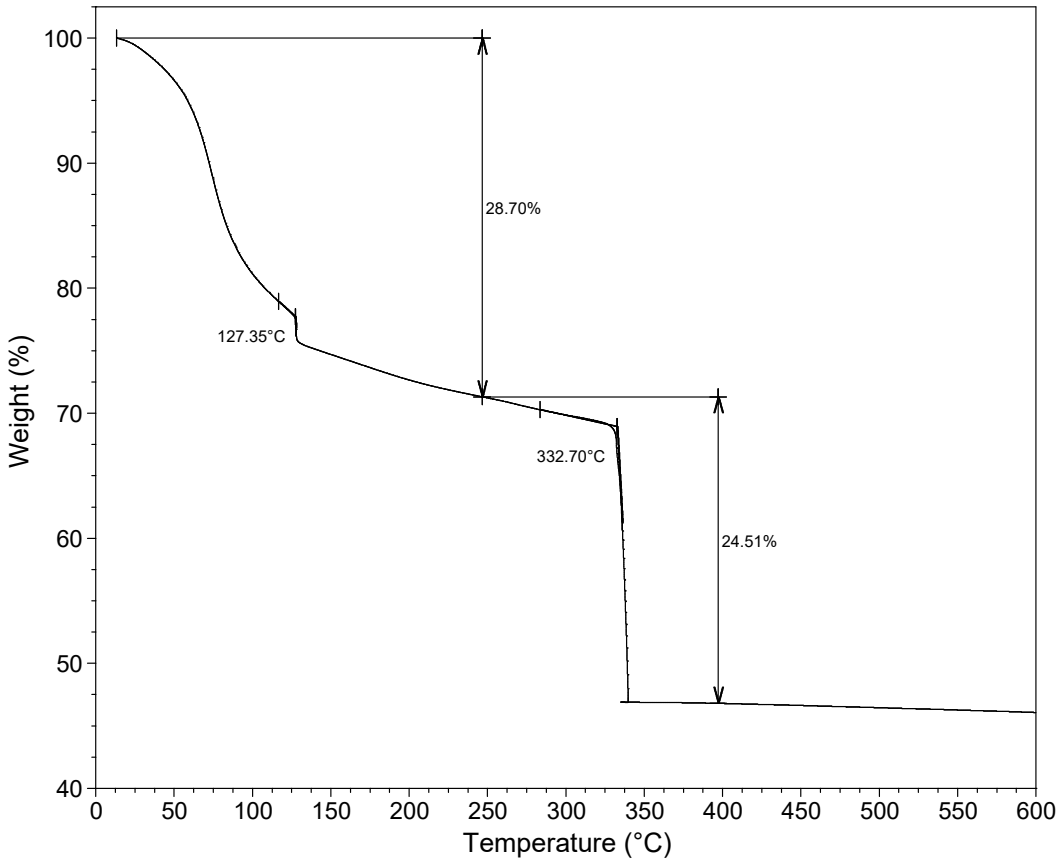

Figure S15. Thermogram of trimanganese bis(hexakis(cyano)cobaltate) ozonized and saturated with methanol.

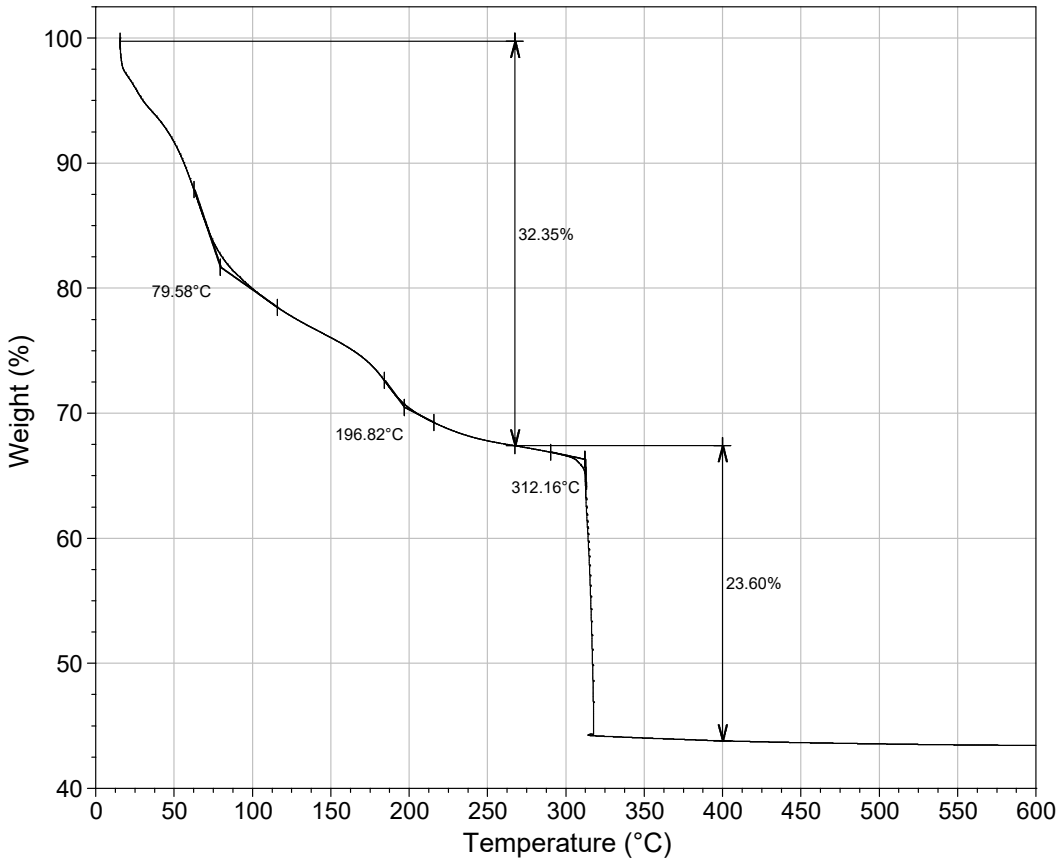

Figure S16. Thermogram of tricobalt bis(hexakis(cyano)cobaltate) ozonized and saturated with methanol.

References

1. Beall, G.W.; Milligan, W.O.; Korp, J.; Bernal, I. Crystal structure of $Mn_3[Co(CN)_6]_2 \cdot 12\,H_2O$ and $Cd_3[Co(CN)_6]_2 \cdot 12\,H_2O$ by neutron and X-ray diffraction. *Inorg. Chem.* **1977**, *16*, 2715–2718.
2. Petric, A.; Ling, H. Electrical Conductivity and Thermal Expansion of Spinels at Elevated Temperatures. *J. Am. Ceram. Soc.* **2007**, *90*, 1515–1520.