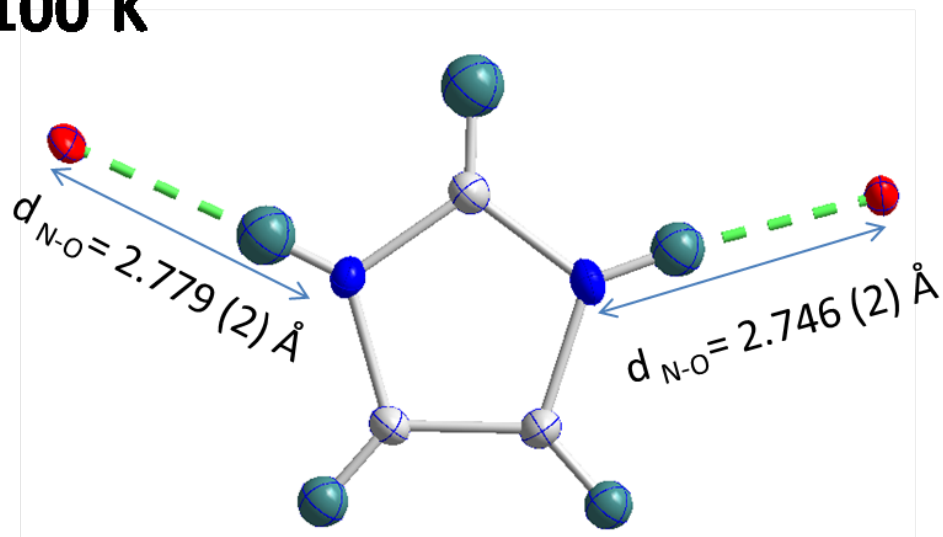


Electronic Supplementary Information

T= 100 K



T= 300 K

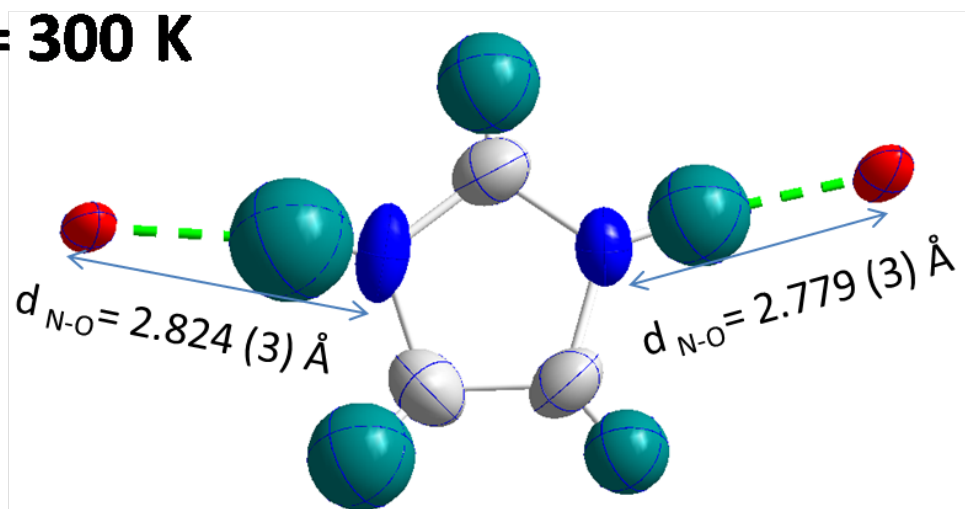


Figure S1. Detail of the imidazolium cation structural parameters, obtained by single-crystal X-ray diffraction. Displacement ellipsoids are represented at the 50% probability level.

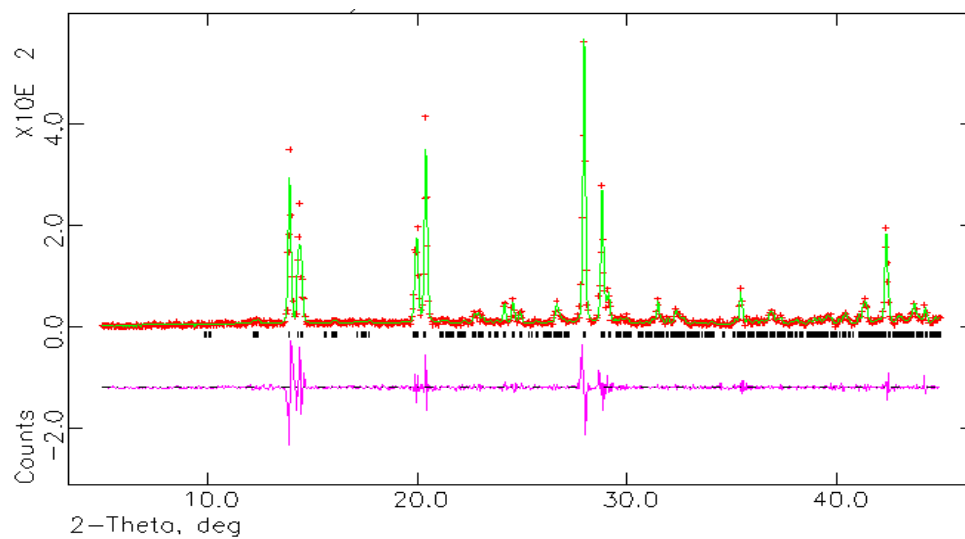


Figure S2.- LeBail refinement of the room temperature powder X-ray diffraction for $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$ Key: observed data (+) and calculated profile (solid line); the difference plot is drawn below the profile. Tick marks indicate peak positions of the $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$ phase.

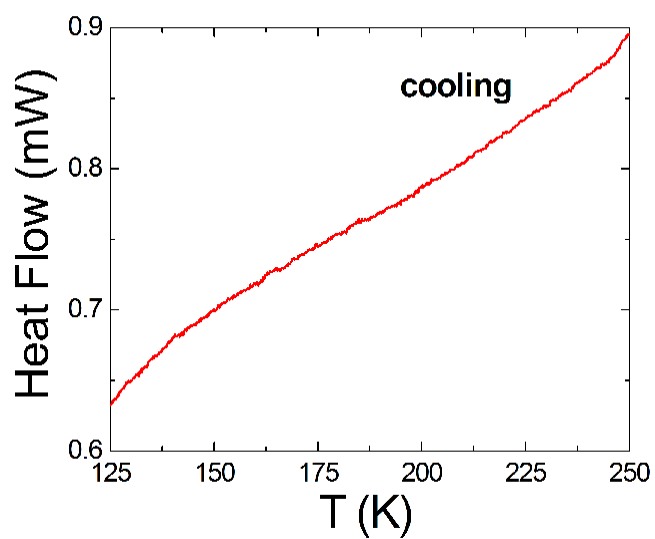


Figure S3. Results of the DSC study of $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$: heat flow as a function of temperature obtained by cooling at a rate of 10 K/min.

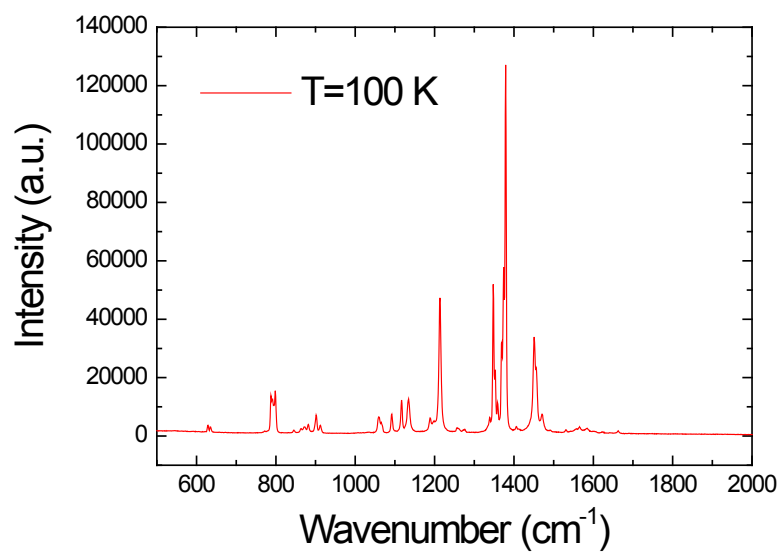


Figure S4. Raman spectra of the $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$ compound recorded at 100 K.

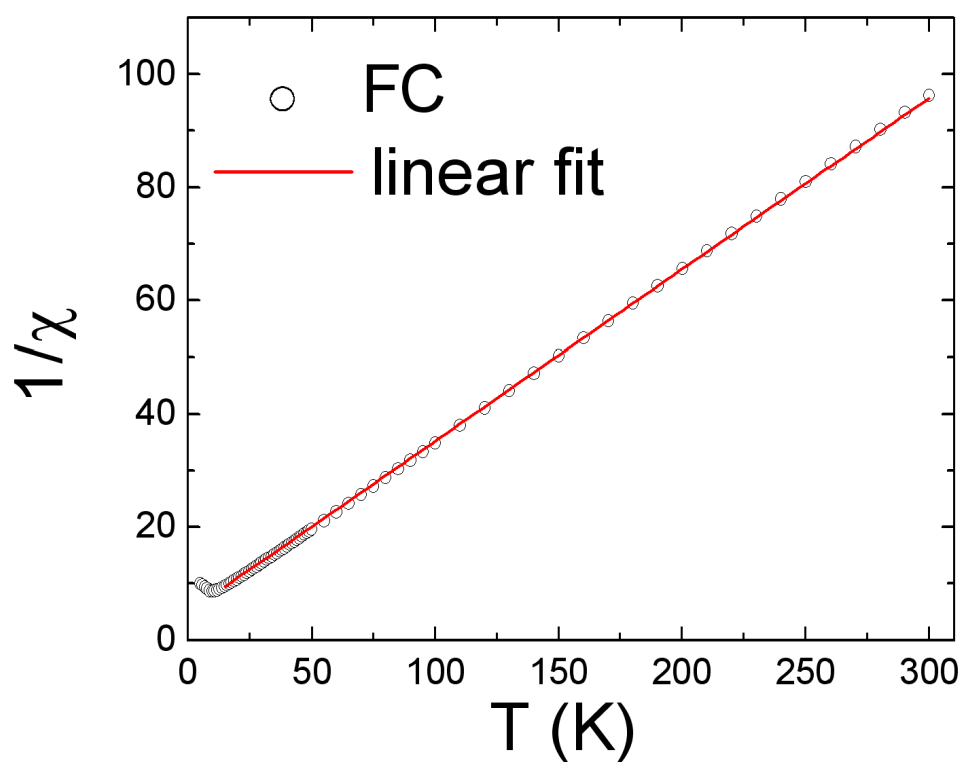


Figure S5.- Plot of the inverse of the magnetic susceptibility (χ) vs. temperature (T) for $(\text{C}_3\text{N}_2\text{H}_5)[\text{Mn}(\text{HCOO})_3]$, measured under an applied magnetic field of 1000 Oe. The line shows the best fitting to the Curie-Weiss law at $T > 20$ K.

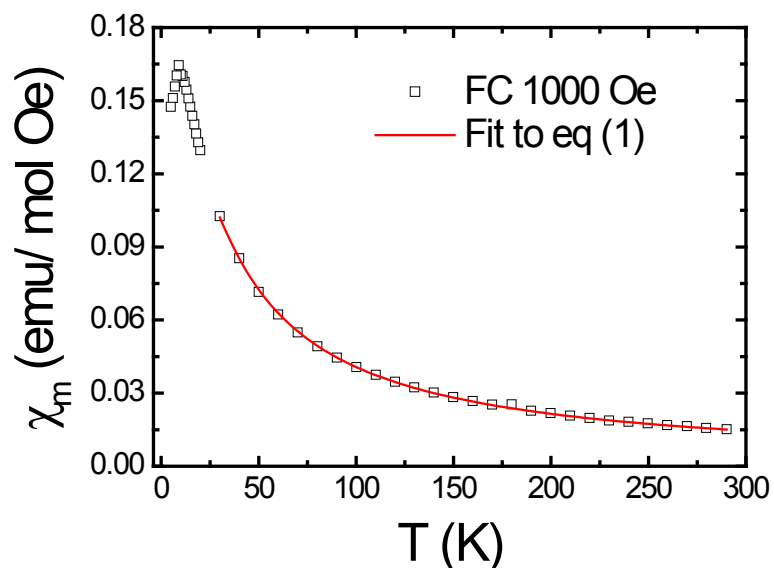


Figure S6.- Plot of the magnetic susceptibility (χ) vs. temperature (T) for $(C_3N_2H_5)[Mn(HCOO)_3]$, measured under an applied magnetic field of 1000 Oe. The solid line shows the best least-squares fitting of the susceptibility data (from 30K to 300 K) using eq. 1.

Table SI Selected bond lengths in Å from the single-crystal X-ray diffraction study at 295 K and at 100 K.

Mn environment			Formate anions		
	100 K	295 K		100 K	295 K
Mn(2)-O(1)	2.200(1)	2.198(2)	C(7)-O(6)	1.247(2)	1.218(3)
Mn(2)-O(4)	2.142(1)	2.140(2)	C(7)-O(11)	1.248(2)	1.233(3)
Mn(2)-O(2)	2.167(1)	2.164(2)	C(8)-O(2)	1.242(2)	1.222(3)
Mn(2)-O(6)	2.156(1)	2.154(2)	C(8)-O(7)	1.258(2)	1.243(3)
Mn(2)-O(3)	2.180(1)	2.180(2)	C(9)-O(1)	1.258(3)	1.240(3)
Mn(2)-O(5)	2.155(1)	2.148(2)	C(9)-O(12)	1.239(3)	1.233(3)
Bond Valence Sum	1.96	1.97	C(10)-O(8)	1.264(2)	1.240(3)
			C(10)-O(5)	1.247(2)	1.233(3)
Mn(1)-O(9)	2.131(1)	2.139(2)	C(11)-O(3)	1.233(2)	1.217(3)
Mn(1)-O(12)	2.171(1)	2.166(2)	C(11)-O(10)	1.265(2)	1.246(3)
Mn(1)-O(7)	2.197(1)	2.195(2)	C(12)-O(4)	1.250(3)	1.233(3)
Mn(1)-O(11)	2.156(1)	2.155(2)	C(12)-O(9)	1.239(3)	1.206(3)
Mn(1)-O(8)	2.180(1)	2.179(2)			
Mn(1)-O(10)	2.179(1)	2.177(2)			
Bond Valence Sum	1.95	1.95			
Imidazolium 1			Imidazolium 2		
	100 K	295 K		100 K	295 K
C(1)-N(1)	1.322(3)	1.291(4)	C(5)-N(4)	1.327(3)	1.317(5)
N(1)-C(2)	1.374(3)	1.344(5)	N(4)-C(4)	1.373(3)	1.338(5)
C(2)-C(3)	1.345(3)	1.328(6)	C(4)-C(6)	1.350(3)	1.323(5)
C(3)-N(2)	1.370(3)	1.350(6)	C(6)-N(5)	1.376(3)	1.351(4)
N(2)-C(1)	1.326(3)	1.292(5)	N(5)-C(5)	1.322(3)	1.321(5)
$d_{N(\text{ImH})-O(\text{formate})}$: H-bond length			$d_{N(\text{ImH})-O(\text{formate})}$: H-bond length		
	100 K	295 K		100 K	295 K
$d_{N-O} \text{ImH}^+(1)$	2.754(2)	2.785(2)	$d_{N-O} \text{ImH}^+(2)$	2.779(2)	2.825(2)
	2.746(2)	2.846(2)		2.746(2)	2.779(2)

Table SII: Vibrational frequencies (in cm^{-1}) obtained by Raman spectroscopy at 100 K for $[(\text{C}_3\text{N}_2\text{H}_5)][\text{Mn}(\text{HCOO})_3]$ and their suggested assignments.

Raman 100 K		Assignment
cm^{-1}	%	
1583	2.3	asym. str. COO^-
1565	2.5	asym. str. COO^-
1529	1.8	asym. str. COO^-
1470	6.3	δ [R]
1456	19.2	ω (R)
1450	28.1	ω (R)
1380	100.0	r (COO^-)
1373	4.7	δ [R]
1368	26.5	δ [R]
1359	9.4	sym. str. COO^-
1353	18.3	sym. str. COO^-
1348	40.9	C-O stretching
1213	39.1	δ [N-H]
1190	4.8	δ [R]
1133	9.8	δ [C-H]
1116	9.7	δ [C-H]
1092	6.1	δ [C-H]
1065	3.9	Rocking (COO^-)
1060	5.3	Rocking (COO^-)
912	3.1	C-H bends out of plane
901	5.6	C-H bends out of plane
882	3.3	ω (C-H)
872	2.5	ω (C-H)
864	2.1	ω (C-H)
845	1.6	ω (C-H)
798	12.5	COO^- deformation
787	11.4	COO^- deformation