. Table S1. Crystal data and structure refinement for 1_330K_a.

Identification code	1_330K_a	
Empirical formula	C5 H16 Cl4 Mn N2	
Formula weight	300.94	
Temperature	330(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Imma	
Unit cell dimensions	a = 23.9162(13) Å	α= 90°.
	b = 7.1877(4) Å	β= 90°.
	c = 7.3898(3) Å	γ = 90°.
Volume	1270.32(11) $Å^3$	
Z	4	
Density (calculated)	1.574 Mg/m^3	
Absorption coefficient	1.838 mm^{-1}	
F(000)	612	
Crystal size	0.195 x 0.144 x 0.065 mm^3	
Theta range for data collection	2.885 to 28.291°.	
Index ranges	-20<=h<=31, -9<=k<=9, -9<=l<=9	
Reflections collected	5258	
Independent reflections	863 [R(int) = 0.0304]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6389	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	863 / 0 / 38	
Goodness-of-fit on F^2	1.118	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0957	
R indices (all data)	R1 = 0.0330, wR2 = 0.0974	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.326 and -0.455 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1_330K_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	7500	7500	2500	28(1)
Cl(1)	7395(1)	5000	0	39(1)
Cl(2)	6468(1)	7500	2943(1)	45(1)
N(1)	6564(1)	7500	7287(4)	50(1)
C(1)	6037(2)	7500	8172(5)	73(1)
C(2)	5531(2)	7500	7196(6)	90(2)
C(3)	5000	7500	8119(9)	73(2)

Table S3. Bond lengths [Å] and angles [°] for 1_330K_a.

Mn(1)-Cl(2)	2.4903(7)
Mn(1)-Cl(2)#1	2.4904(7)
Mn(1)-Cl(1)#1	2.58945(11)
Mn(1)-Cl(1)#2	2.58945(11)
Mn(1)-Cl(1)#3	2.58945(11)
Mn(1)-Cl(1)	2.58945(11)
N(1)-C(1)	1.421(5)
N(1)-H(1A)	0.8900
N(1)-H(1B)	0.8900
N(1)-H(1C)	0.8900
C(1)-C(2)	1.409(5)
C(1)-H(1D)	0.9700
C(1)-H(1E)	0.9700
C(2)-C(3)	1.441(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700

Cl(2)-Mn(1)-Cl(2)#1	180.0
Cl(2)-Mn(1)-Cl(1)#1	90.14(2)
Cl(2)#1-Mn(1)-Cl(1)#1	89.86(2)
Cl(2)-Mn(1)-Cl(1)#2	89.86(2)
Cl(2)#1-Mn(1)-Cl(1)#2	90.14(2)
Cl(1)#1-Mn(1)-Cl(1)#2	92.114(5)
Cl(2)-Mn(1)-Cl(1)#3	90.14(2)
Cl(2)#1-Mn(1)-Cl(1)#3	89.86(2)
Cl(1)#1-Mn(1)-Cl(1)#3	87.886(5)
Cl(1)#2-Mn(1)-Cl(1)#3	180.0
Cl(2)-Mn(1)-Cl(1)	89.86(2)
Cl(2)#1-Mn(1)-Cl(1)	90.14(2)
Cl(1)#1-Mn(1)-Cl(1)	180.0
Cl(1)#2-Mn(1)-Cl(1)	87.886(5)

Cl(1)#3-Mn(1)-Cl(1)	92.114(5)
Mn(1)-Cl(1)-Mn(1)#4	168.85(3)
C(1)-N(1)-H(1A)	109.5
C(1)-N(1)-H(1B)	109.5
H(1A)-N(1)-H(1B)	109.5
C(1)-N(1)-H(1C)	109.5
H(1A)-N(1)-H(1C)	109.5
H(1B)-N(1)-H(1C)	109.5
C(2)-C(1)-N(1)	121.8(3)
C(2)-C(1)-H(1D)	106.9
N(1)-C(1)-H(1D)	106.9
C(2)-C(1)-H(1E)	106.9
N(1)-C(1)-H(1E)	106.9
H(1D)-C(1)-H(1E)	106.7
C(1)-C(2)-C(3)	120.9(4)
C(1)-C(2)-H(2A)	107.1
C(3)-C(2)-H(2A)	107.1
C(1)-C(2)-H(2B)	107.1
C(3)-C(2)-H(2B)	107.1
H(2A)-C(2)-H(2B)	106.8
C(2)#5-C(3)-C(2)	123.5(6)
C(2)#5-C(3)-H(3A)	106.5
C(2)-C(3)-H(3A)	106.5
C(2)#5-C(3)-H(3B)	106.5
C(2)-C(3)-H(3B)	106.5
H(3A)-C(3)-H(3B)	106.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,-y+3/2,-z+1/2 #2 x,y+1/2,-z #3 -x+3/2,-y+1,z+1/2

#4 -x+3/2,-y+1,z-1/2 #5 -x+1,-y+3/2,z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1_330K_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	33(1)	26(1)	24(1)	0	1(1)	0
Cl(1)	51(1)	32(1)	33(1)	-10(1)	0	0
Cl(2)	33(1)	64(1)	37(1)	0	0(1)	0
N(1)	34(1)	75(2)	42(1)	0	-4(1)	0
C(1)	33(2)	140(4)	46(2)	0	1(2)	0
C(2)	32(2)	179(7)	57(2)	0	0(2)	0
C(3)	35(2)	122(6)	63(3)	0	0	0

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1_330K_a.

	x	y	z	U(eq)
H(1A)	6836	7500	8110	75
H(1B)	6593	6489	6598	75
H(1C)	6593	8511	6598	75
H(1D)	6030	6417	8956	88
H(1E)	6030	8583	8956	88
H(2A)	5536	6417	6413	108
H(2B)	5536	8583	6413	108
H(3A)	5000	6419	8904	88
H(3B)	5000	8581	8904	88