. Table S1. Crystal data and structure refinement for Imma_a.

Identification code	Imma_a	
Empirical formula	C5 H16 Cl4 Mn N2	
Formula weight	300.94	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Imma	
Unit cell dimensions	a = 24.1756(9) Å	α= 90°.
	b = 7.1535(3) Å	β= 90°.
	c = 7.3314(3) Å	γ = 90°.
Volume	1267.89(9) $Å^3$	
Z	4	
Density (calculated)	1.577 Mg/m^3	
Absorption coefficient	1.842 mm^{-1}	
F(000)	612	
Crystal size	0.213 x 0.156 x 0.105 mm^3	
Theta range for data collection	2.903 to 28.317°.	
Index ranges	-31<=h<=32, -7<=k<=9, -9<=l<=9	
Reflections collected	5418	
Independent reflections	867 [R(int) = 0.0413]	
Completeness to theta = 25.242°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6588	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	867 / 0 / 38	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1178	
R indices (all data)	R1 = 0.0394, wR2 = 0.1190	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.593 and -0.957 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Mn(1)	2500	2500	7500	13(1)
Cl(1)	3524(1)	2500	7031(1)	24(1)
Cl(2)	2613(1)	5000	10000	35(1)
N(1)	3443(1)	2500	2687(5)	34(1)
C(1)	5000	2500	1875(9)	46(2)
C(2)	3968(2)	2500	1827(6)	55(2)
C(3)	4472(2)	2500	2773(7)	70(3)

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

Mn(1)-Cl(1)	2.4984(8)
Mn(1)-Cl(1)#1	2.4984(8)
Mn(1)-Cl(2)#1	2.57524(12)
Mn(1)-Cl(2)#2	2.57524(12)
Mn(1)-Cl(2)#3	2.57524(12)
Mn(1)-Cl(2)	2.57524(12)
N(1)-C(2)	1.417(5)
N(1)-H(1NA)	0.9100
N(1)-H(1NB)	0.9100
N(1)-H(1NC)	0.9100
C(1)-C(3)	1.436(5)
C(1)-C(3)#4	1.436(5)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.403(6)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900

Cl(1)-Mn(1)-Cl(1)#1	180.0
Cl(1)-Mn(1)-Cl(2)#1	90.39(2)
Cl(1)#1-Mn(1)-Cl(2)#1	89.61(2)
Cl(1)-Mn(1)-Cl(2)#2	89.61(2)
Cl(1)#1-Mn(1)-Cl(2)#2	90.39(2)
Cl(2)#1-Mn(1)-Cl(2)#2	92.033(5)
Cl(1)-Mn(1)-Cl(2)#3	90.39(2)
Cl(1)#1-Mn(1)-Cl(2)#3	89.61(2)
Cl(2)#1-Mn(1)-Cl(2)#3	87.967(5)
Cl(2)#2-Mn(1)-Cl(2)#3	180.0
Cl(1)-Mn(1)-Cl(2)	89.60(2)
Cl(1)#1-Mn(1)-Cl(2)	90.40(2)
Cl(2)#1-Mn(1)-Cl(2)	180.0

Cl(2)#2-Mn(1)-Cl(2)	87.967(5)
Cl(2)#3-Mn(1)-Cl(2)	92.033(5)
Mn(1)-Cl(2)-Mn(1)#5	167.85(4)
C(2)-N(1)-H(1NA)	109.5
C(2)-N(1)-H(1NB)	109.5
H(1NA)-N(1)-H(1NB)	109.5
C(2)-N(1)-H(1NC)	109.5
H(1NA)-N(1)-H(1NC)	109.5
H(1NB)-N(1)-H(1NC)	109.5
C(3)-C(1)-C(3)#4	125.4(6)
C(3)-C(1)-H(1A)	106.0
C(3)#4-C(1)-H(1A)	106.0
C(3)-C(1)-H(1B)	106.0
C(3)#4-C(1)-H(1B)	106.0
H(1A)-C(1)-H(1B)	106.3
C(3)-C(2)-N(1)	123.9(4)
C(3)-C(2)-H(2A)	106.3
N(1)-C(2)-H(2A)	106.3
C(3)-C(2)-H(2B)	106.3
N(1)-C(2)-H(2B)	106.3
H(2A)-C(2)-H(2B)	106.4
C(2)-C(3)-C(1)	123.1(5)
C(2)-C(3)-H(3A)	106.6
C(1)-C(3)-H(3A)	106.6
C(2)-C(3)-H(3B)	106.6
C(1)-C(3)-H(3B)	106.6
H(3A)-C(3)-H(3B)	106.5

Symmetry transformations used to generate equivalent atoms:

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

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

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Imma_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)	15(1)	12(1)	12(1)	0	1(1)	0
Cl(1)	15(1)	37(1)	18(1)	0	0(1)	0
Cl(2)	21(1)	41(1)	44(1)	-32(1)	0	0
N(1)	16(2)	64(3)	21(2)	0	-2(1)	0
C(1)	17(3)	92(6)	29(3)	0	0	0
C(2)	16(2)	129(6)	21(2)	0	1(2)	0
C(3)	15(2)	167(9)	28(2)	0	1(2)	0

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

	x	y	z	U(eq)
H(1NA)	3173	2500	1824	50
H(1NB)	3410	1461	3395	50
H(1NC)	3410	3539	3395	50
H(1A)	5000	3607	1065	55
H(1B)	5000	1393	1065	55
H(2A)	3975	1392	1019	66
H(2B)	3975	3608	1019	66
H(3A)	4467	1391	3581	84
H(3B)	4467	3609	3581	84