

Supporting Information
for
New Binuclear Mn^{II} and Fe^{II} Complexes Supported by 1,4,8-
Triazacycloundecane

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Crystallographic Information for $[\text{Fe}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (1)

Data collection

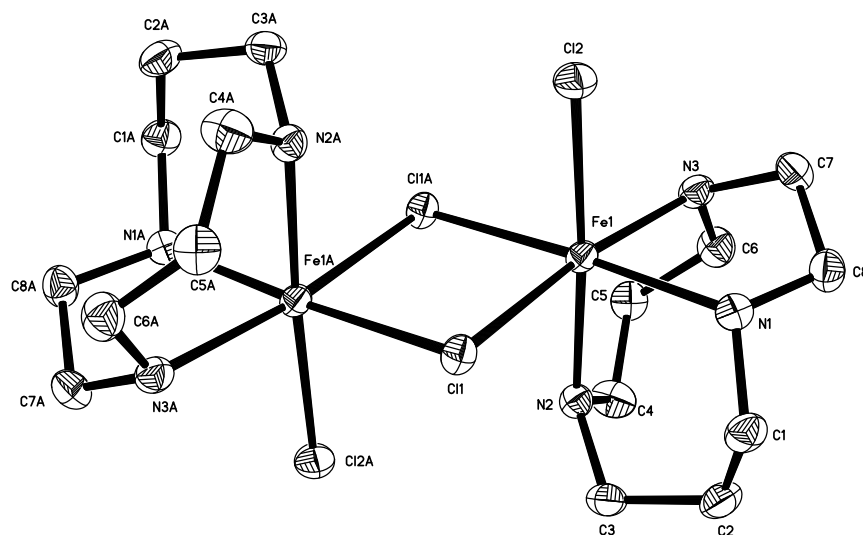
A crystal (approximate dimensions $0.40 \times 0.20 \times 0.20 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for a data collection at $173(2) \text{ K}$.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 50 reflections. The data collection was carried out using $\text{MoK}\alpha$ radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.978 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.78 \AA . Four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from the xyz centroids of 2216 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

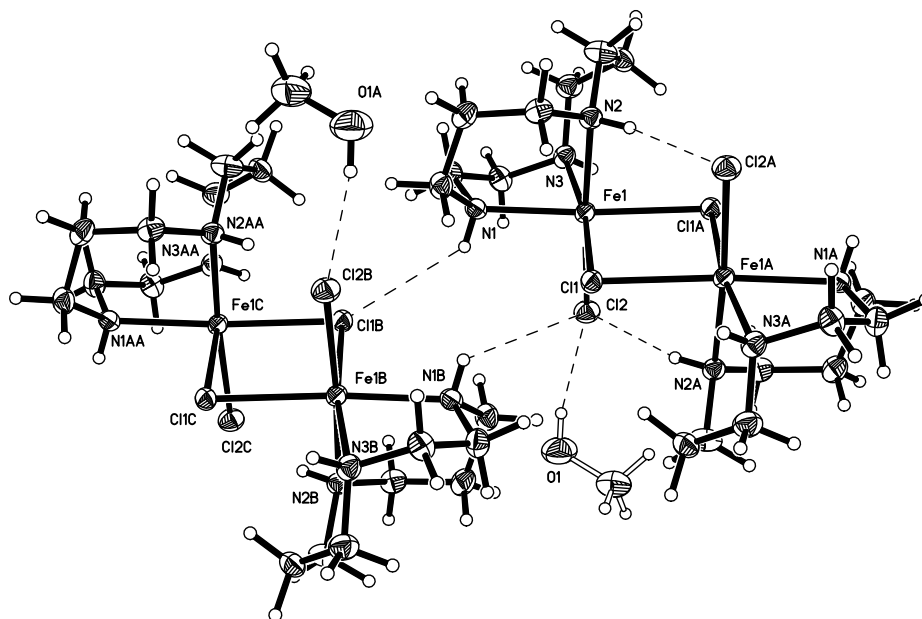
Structure solution and refinement

The structure was solved using SHELXS-97⁴ and refined using SHELXL-97.⁴ The space group $P-1$ was determined based on the lack of systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The protons on N1 N2 and N3 were placed from the difference map and were with anisotropic displacement parameters. All remaining hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0230$ and $wR2 = 0.0626$ (F^2 , all data).

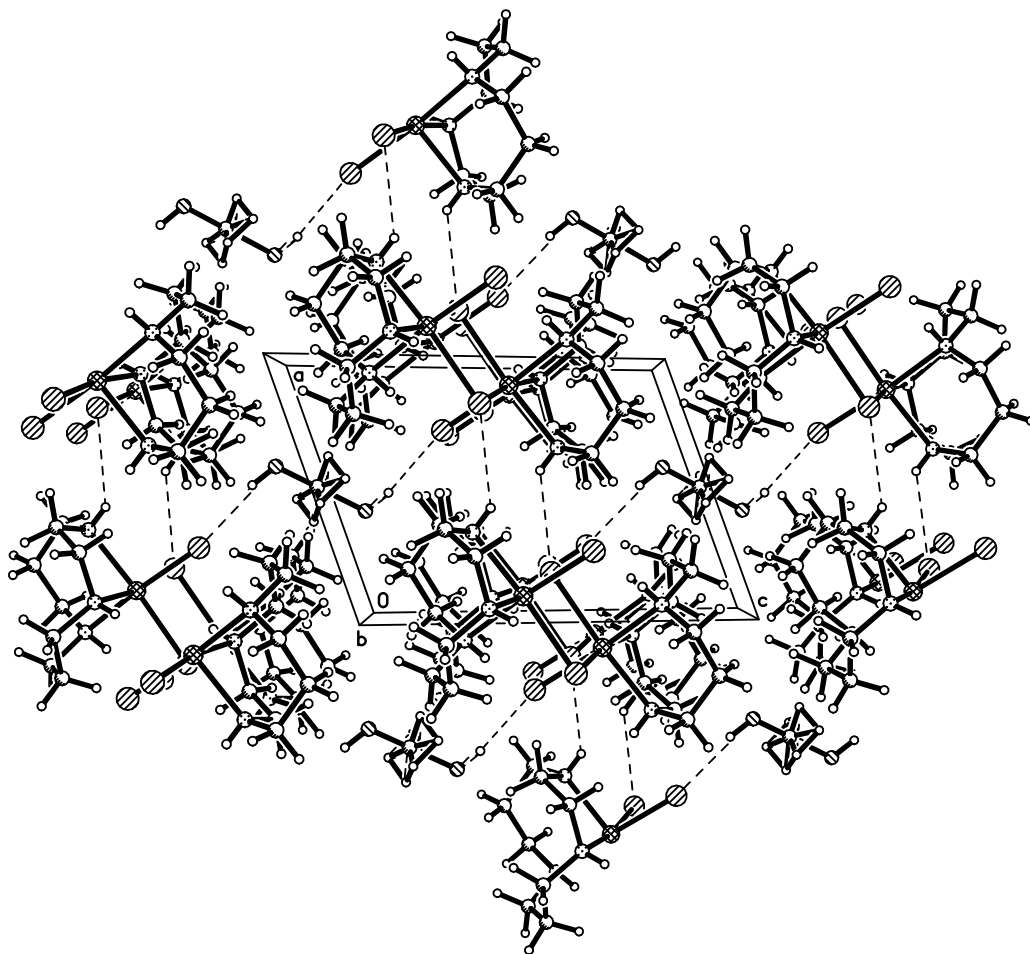
Structure description

The structure is the one suggested. The molecule lies over an inversion center. The methanol molecule was modeled as disordered over an inversion center and the oxygen-carbon distance was fixed to 1.41 (0.01) with a soft DFIX restraint. Hydrogen bonding exists between the proton on N1 and C11; the proton on N2 and both C11 and C12; the proton on N3 and C12; and the proton on O1 and C12.





Hydrogen bonding interactions



Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Benjamin E. Kucera as a coauthor or 2) acknowledge Benjamin E. Kucera, Victor G. Young, Jr., and the X-Ray Crystallographic Laboratory.

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- 1 SMART V5.054, Bruker Analytical X-ray Systems, Madison, WI (2001).
 - 2 An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33-38 (1995).
 - 3 SAINT+ V6.45, Bruker Analytical X-Ray Systems, Madison, WI (2003).
 - 4 SHELXTL V6.14, Bruker Analytical X-Ray Systems, Madison, WI (2000).

Some equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q / [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

Table S8. Crystal data and structure refinement for $[\text{Fe}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (**1**).

Identification code	05357	
Empirical formula	$\text{C}_{17}\text{H}_{42}\text{Cl}_4\text{Fe}_2\text{N}_6\text{O}$	
Formula weight	600.07	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	$a = 7.7321(12)$ Å	$\alpha = 107.832(2)^\circ$
	$b = 7.8896(12)$ Å	$\beta = 107.827(2)^\circ$
	$c = 11.4945(17)$ Å	$\gamma = 92.642(2)^\circ$
Volume	$627.85(17)$ Å ³	
<i>Z</i>	1	
Density (calculated)	1.587 Mg/m ³	
Absorption coefficient	1.603 mm ⁻¹	
<i>F</i> (000)	314	
Crystal color, morphology	colorless, block	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.98 to 27.15°	
Index ranges	$-9 \leq h \leq 9, -10 \leq k \leq 10, -14 \leq l \leq 14$	
Reflections collected	7159	
Independent reflections	2725 [<i>R</i> (int) = 0.0201]	
Observed reflections	2469	
Completeness to theta = 27.15°	98.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7399 and 0.5665	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2725 / 1 / 158	
Goodness-of-fit on <i>F</i> ²	1.052	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0230, <i>wR</i> 2 = 0.0596	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0271, <i>wR</i> 2 = 0.0626	
Largest diff. peak and hole	0.533 and -0.237 e.Å ⁻³	

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Fe}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (**1**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe1	1040(1)	1284(1)	4241(1)	18(1)
Cl1	1820(1)	-1295(1)	5142(1)	20(1)
N1	3406(2)	1133(2)	3560(1)	20(1)
C1	3657(2)	-668(2)	2780(2)	26(1)
C2	1986(2)	-1651(2)	1594(2)	29(1)
C3	312(2)	-2302(2)	1860(2)	25(1)
N2	-649(2)	-818(2)	2382(1)	20(1)
C4	-1896(3)	-306(2)	1315(2)	30(1)
C5	-2258(2)	1622(2)	1709(2)	26(1)
C6	-609(2)	2997(2)	2011(2)	29(1)
N3	695(2)	3427(2)	3342(1)	23(1)
C7	2596(2)	4095(2)	3453(2)	25(1)
C8	3533(2)	2514(2)	2945(2)	26(1)
Cl2	2737(1)	3559(1)	6353(1)	26(1)
O1	5861(4)	5533(5)	9097(3)	51(1)
C9	5080(40)	5060(40)	9930(30)	44(1)

Table S10. Bond lengths [Å] and angles [°] for [Fe₂(tacud)₂(μ-Cl)₂Cl₂] (1).

Fe(1)-N(1)	2.1947(14)	C(7)-H(7B)	0.9900
Fe(1)-N(3)	2.2226(14)	C(8)-H(8A)	0.9900
Fe(1)-N(2)	2.2229(14)	C(8)-H(8B)	0.9900
Fe(1)-Cl(2)	2.4499(5)	O(1)-C(9)	1.405(10)
Fe(1)-Cl(1)#1	2.5203(5)	O(1)-H(1C)	0.8400
Fe(1)-Cl(1)	2.5690(5)	C(9)-H(9A)	0.9800
Cl(1)-Fe(1)#1	2.5203(5)	C(9)-H(9B)	0.9800
N(1)-C(8)	1.483(2)	C(9)-H(9C)	0.9800
N(1)-C(1)	1.487(2)		
N(1)-H(1N)	0.81(2)	N(1)-Fe(1)-N(3)	79.87(5)
C(1)-C(2)	1.520(2)	N(1)-Fe(1)-N(2)	89.73(5)
C(1)-H(1A)	0.9900	N(3)-Fe(1)-N(2)	91.99(5)
C(1)-H(1B)	0.9900	N(1)-Fe(1)-Cl(2)	94.09(4)
C(2)-C(3)	1.520(2)	N(3)-Fe(1)-Cl(2)	89.77(4)
C(2)-H(2A)	0.9900	N(2)-Fe(1)-Cl(2)	176.02(4)
C(2)-H(2B)	0.9900	N(1)-Fe(1)-Cl(1)#1	175.72(4)
C(3)-N(2)	1.485(2)	N(3)-Fe(1)-Cl(1)#1	99.88(4)
C(3)-H(3A)	0.9900	N(2)-Fe(1)-Cl(1)#1	86.01(4)
C(3)-H(3B)	0.9900	Cl(2)-Fe(1)-Cl(1)#1	90.174(17)
N(2)-C(4)	1.487(2)	N(1)-Fe(1)-Cl(1)	91.77(4)
N(2)-H(2N)	0.85(2)	N(3)-Fe(1)-Cl(1)	171.59(4)
C(4)-C(5)	1.514(2)	N(2)-Fe(1)-Cl(1)	87.00(4)
C(4)-H(4A)	0.9900	Cl(2)-Fe(1)-Cl(1)	91.771(18)
C(4)-H(4B)	0.9900	Cl(1)#1-Fe(1)-Cl(1)	88.383(14)
C(5)-C(6)	1.515(2)	Fe(1)#1-Cl(1)-Fe(1)	91.617(14)
C(5)-H(5A)	0.9900	C(8)-N(1)-C(1)	112.34(13)
C(5)-H(5B)	0.9900	C(8)-N(1)-Fe(1)	110.98(10)
C(6)-N(3)	1.476(2)	C(1)-N(1)-Fe(1)	117.81(10)
C(6)-H(6A)	0.9900	C(8)-N(1)-H(1N)	104.2(15)
C(6)-H(6B)	0.9900	C(1)-N(1)-H(1N)	105.4(15)
N(3)-C(7)	1.493(2)	Fe(1)-N(1)-H(1N)	104.8(15)
N(3)-H(3N)	0.87(2)	N(1)-C(1)-C(2)	113.90(13)
C(7)-C(8)	1.522(2)	N(1)-C(1)-H(1A)	108.8
C(7)-H(7A)	0.9900	C(2)-C(1)-H(1A)	108.8

N(1)-C(1)-H(1B)	108.8	C(4)-C(5)-H(5B)	108.9
C(2)-C(1)-H(1B)	108.8	C(6)-C(5)-H(5B)	108.9
H(1A)-C(1)-H(1B)	107.7	H(5A)-C(5)-H(5B)	107.7
C(1)-C(2)-C(3)	116.12(14)	N(3)-C(6)-C(5)	112.74(14)
C(1)-C(2)-H(2A)	108.3	N(3)-C(6)-H(6A)	109.0
C(3)-C(2)-H(2A)	108.3	C(5)-C(6)-H(6A)	109.0
C(1)-C(2)-H(2B)	108.3	N(3)-C(6)-H(6B)	109.0
C(3)-C(2)-H(2B)	108.3	C(5)-C(6)-H(6B)	109.0
H(2A)-C(2)-H(2B)	107.4	H(6A)-C(6)-H(6B)	107.8
N(2)-C(3)-C(2)	113.13(13)	C(6)-N(3)-C(7)	111.84(13)
N(2)-C(3)-H(3A)	109.0	C(6)-N(3)-Fe(1)	119.04(10)
C(2)-C(3)-H(3A)	109.0	C(7)-N(3)-Fe(1)	104.60(10)
N(2)-C(3)-H(3B)	109.0	C(6)-N(3)-H(3N)	104.4(14)
C(2)-C(3)-H(3B)	109.0	C(7)-N(3)-H(3N)	109.3(14)
H(3A)-C(3)-H(3B)	107.8	Fe(1)-N(3)-H(3N)	107.4(14)
C(3)-N(2)-C(4)	110.79(13)	N(3)-C(7)-C(8)	110.00(13)
C(3)-N(2)-Fe(1)	115.39(10)	N(3)-C(7)-H(7A)	109.7
C(4)-N(2)-Fe(1)	120.55(10)	C(8)-C(7)-H(7A)	109.7
C(3)-N(2)-H(2N)	107.7(14)	N(3)-C(7)-H(7B)	109.7
C(4)-N(2)-H(2N)	105.8(14)	C(8)-C(7)-H(7B)	109.7
Fe(1)-N(2)-H(2N)	93.9(14)	H(7A)-C(7)-H(7B)	108.2
N(2)-C(4)-C(5)	114.84(14)	N(1)-C(8)-C(7)	110.98(13)
N(2)-C(4)-H(4A)	108.6	N(1)-C(8)-H(8A)	109.4
C(5)-C(4)-H(4A)	108.6	C(7)-C(8)-H(8A)	109.4
N(2)-C(4)-H(4B)	108.6	N(1)-C(8)-H(8B)	109.4
C(5)-C(4)-H(4B)	108.6	C(7)-C(8)-H(8B)	109.4
H(4A)-C(4)-H(4B)	107.5	H(8A)-C(8)-H(8B)	108.0
C(4)-C(5)-C(6)	113.56(14)	C(9)-O(1)-H(1C)	109.5
C(4)-C(5)-H(5A)	108.9		
C(6)-C(5)-H(5A)	108.9		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table S11. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Fe}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (**1**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^* U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	20(1)	19(1)	16(1)	7(1)	7(1)	5(1)
Cl1	19(1)	24(1)	21(1)	11(1)	9(1)	8(1)
N1	18(1)	22(1)	20(1)	7(1)	5(1)	4(1)
C1	25(1)	26(1)	29(1)	9(1)	13(1)	11(1)
C2	33(1)	29(1)	24(1)	4(1)	14(1)	7(1)
C3	30(1)	18(1)	23(1)	4(1)	8(1)	4(1)
N2	22(1)	21(1)	20(1)	9(1)	7(1)	5(1)
C4	33(1)	27(1)	24(1)	9(1)	0(1)	4(1)
C5	20(1)	31(1)	29(1)	13(1)	6(1)	8(1)
C6	32(1)	31(1)	26(1)	14(1)	8(1)	5(1)
N3	26(1)	22(1)	23(1)	7(1)	11(1)	8(1)
C7	23(1)	21(1)	32(1)	10(1)	9(1)	2(1)
C8	25(1)	27(1)	32(1)	14(1)	14(1)	7(1)
Cl2	29(1)	24(1)	21(1)	3(1)	6(1)	0(1)
O1	50(2)	59(2)	34(2)	12(1)	3(1)	-8(2)
C9	47(5)	43(3)	37(5)	15(3)	5(2)	10(3)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Fe}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (**1**).

	x	y	z	U(eq)
H1N	4290(30)	1450(30)	4210(20)	32(5)
H1A	3953	-1422	3341	31
H1B	4720	-517	2492	31
H2A	2352	-2706	1046	34
H2B	1623	-837	1085	34
H3A	-561	-3169	1044	29
H3B	702	-2948	2490	29
H2N	-1340(30)	-1220(30)	2720(20)	32(5)
H4A	-3086	-1120	953	36
H4B	-1357	-501	615	36
H5A	-2640	1872	2484	31
H5B	-3290	1761	998	31
H6A	38	2527	1384	35
H6B	-1040	4117	1897	35
H3N	280(30)	4290(30)	3820(20)	36(6)
H7A	3315	4778	4372	30
H7B	2544	4916	2946	30
H8A	2944	1966	1993	31
H8B	4842	2952	3131	31
H1C	5145	5075	8327	77
H9A	5551	4000	10102	66
H9B	3737	4787	9519	66
H9C	5395	6069	10748	66

Table S13. Torsion angles [°] for [Fe₂(tacud)₂(μ-Cl)₂Cl₂] (**1**).

N1-Fe1-Cl1-Fe1#1	-175.72(4)	C4-C5-C6-N3	-82.28(18)
N3-Fe1-Cl1-Fe1#1	-169.4(3)	C5-C6-N3-C7	155.17(14)
N2-Fe1-Cl1-Fe1#1	-86.09(4)	C5-C6-N3-Fe1	32.96(18)
Cl2-Fe1-Cl1-Fe1#1	90.124(17)	N1-Fe1-N3-C6	97.87(12)
Cl1#1-Fe1-Cl1-Fe1#1	0.0	N2-Fe1-N3-C6	8.49(12)
N3-Fe1-N1-C8	2.07(11)	Cl2-Fe1-N3-C6	-167.94(12)
N2-Fe1-N1-C8	94.14(11)	Cl1#1-Fe1-N3-C6	-77.80(12)
Cl2-Fe1-N1-C8	-86.97(10)	Cl1-Fe1-N3-C6	91.4(3)
Cl1#1-Fe1-N1-C8	89.1(5)	N1-Fe1-N3-C7	-27.89(10)
Cl1-Fe1-N1-C8	-178.87(10)	N2-Fe1-N3-C7	-117.26(10)
N3-Fe1-N1-C1	-129.43(12)	Cl2-Fe1-N3-C7	66.31(10)
N2-Fe1-N1-C1	-37.36(12)	Cl1#1-Fe1-N3-C7	156.44(9)
Cl2-Fe1-N1-C1	141.54(11)	Cl1-Fe1-N3-C7	-34.3(3)
Cl1#1-Fe1-N1-C1	-42.4(6)	C6-N3-C7-C8	-80.06(17)
Cl1-Fe1-N1-C1	49.64(11)	Fe1-N3-C7-C8	50.09(15)
C8-N1-C1-C2	-76.21(18)	C1-N1-C8-C7	158.84(14)
Fe1-N1-C1-C2	54.67(17)	Fe1-N1-C8-C7	24.59(16)
N1-C1-C2-C3	-69.16(19)	N3-C7-C8-N1	-51.51(18)
C1-C2-C3-N2	72.70(19)		
C2-C3-N2-C4	81.88(17)		
C2-C3-N2-Fe1	-59.56(16)	Symmetry transformations used to generate equivalent atoms:	
N1-Fe1-N2-C3	39.39(11)	#1 -x,-y,-z+1	
N3-Fe1-N2-C3	119.25(11)		
Cl2-Fe1-N2-C3	-124.5(5)		
Cl1#1-Fe1-N2-C3	-140.98(11)		
Cl1-Fe1-N2-C3	-52.40(11)		
N1-Fe1-N2-C4	-98.02(13)		
N3-Fe1-N2-C4	-18.17(13)		
Cl2-Fe1-N2-C4	98.1(5)		
Cl1#1-Fe1-N2-C4	81.60(12)		
Cl1-Fe1-N2-C4	170.19(12)		
C3-N2-C4-C5	-153.39(15)		
Fe1-N2-C4-C5	-14.2(2)		
N2-C4-C5-C6	70.5(2)		

Table S14. Hydrogen bonds for [Fe₂(tacud)₂(μ-Cl)₂Cl₂] (**1**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1N...Cl1#2	0.81(2)	2.88(2)	3.5116(15)	136.2(18)
N2-H2N...Cl2#1	0.85(2)	2.73(2)	3.5276(15)	157.3(18)
N2-H2N...Cl1#1	0.85(2)	2.79(2)	3.2424(14)	115.5(16)
N3-H3N...Cl2#3	0.87(2)	2.94(2)	3.6686(15)	142.0(18)
O1-H1C...Cl2	0.84	2.37	3.192(3)	168.3

Symmetry transformations used to generate equivalent atoms:

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

Crystallographic Data for $[\text{Mn}_2(\text{tacud})_2(\mu\text{-Cl})_2\text{Cl}_2]$ (2)

Data collection

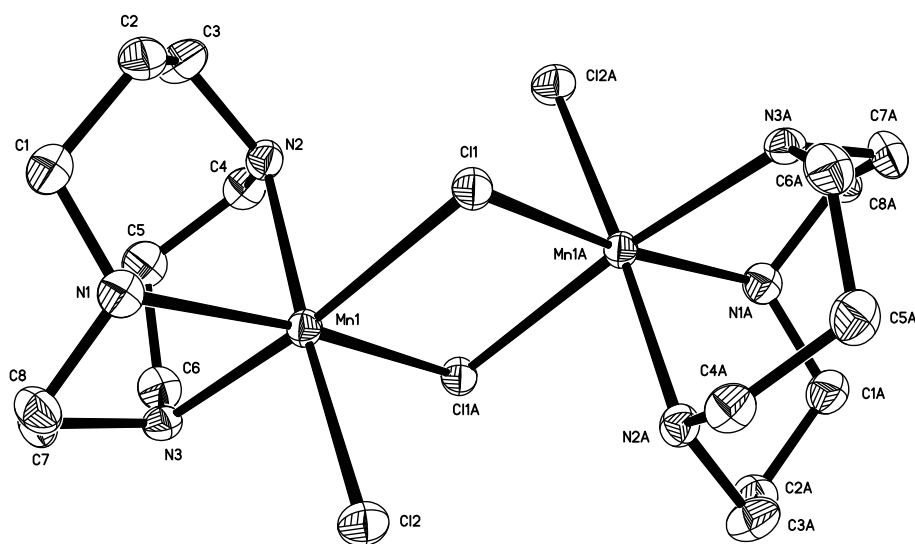
A crystal (approximate dimensions $0.30 \times 0.15 \times 0.05 \text{ mm}^3$) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for a data collection at 173(2) K.¹ A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 61 reflections. The data collection was carried out using MoK α radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 4.913 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30° steps in ω at four different ϕ settings and a detector position of -28° in 2θ . The intensity data were corrected for absorption and decay (SADABS).² Final cell constants were calculated from the xyz centroids of 2433 strong reflections from the actual data collection after integration (SAINT).³ Please refer to Table 1 for additional crystal and refinement information.

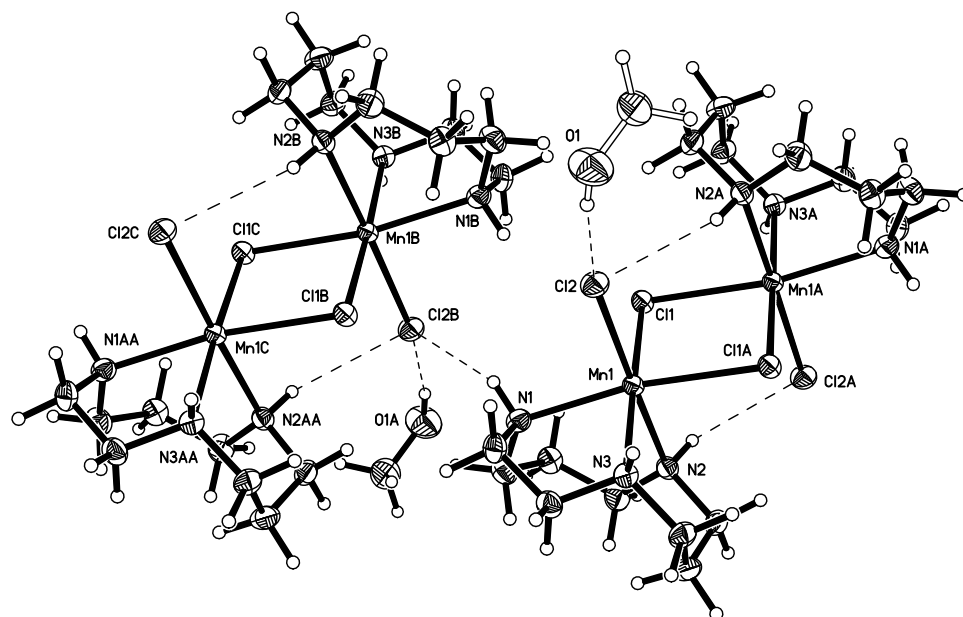
Structure solution and refinement

The structure was solved using SHELXS-97⁴ and refined using SHELXL-97.⁴ The space group *P*-1 was determined based on the lack of systematic absences and intensity statistics. A Patterson Map solution was calculated which provided the position of the Mn and Cl atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The protons on N1 N2 and N3 were placed from the difference map and refined with anisotropic displacement parameters. All remaining hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0253$ and $wR2 = 0.0596$ (F^2 , all data).

Structure description

The structure is the one suggested. The molecule lies on an inversion center. The methanol molecule was modeled as disordered over an inversion center, and the carbon-oxygen distance was set to be 1.41 (0.01) using a soft DFIX restraint. Hydrogen bonding exists between the nitrogen protons and the chlorine atoms, as well as between the methanol proton and a chlorine atom.





Picture of Hydrogen Bonding Interactions

