Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Preparation of a "Twisted Basket" Mn_4N_8 cluster: a two-hydrogen-atom reduced analogue of the Mn_4N_8 pinned butterfly.

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Contents.

Experimental

All operations were carried out under rigorous dry, anaerobic conditions using glovebox and Schlenk line techniques. All reagents were purchased and used as obtained from commercial providers (Aldrich, Fisher, Strem) unless otherwise specified. THF and pyridine were purified by distillation from sodium-benzophenone ketyl. Aniline was distilled using CaH_2 as a scavenger. DCM, pentane, toluene, and benzene were purified using a PureSolve solvent purification system. Solvents were degassed and stored over 3 Å molecular sieves for 12 hours before use. Deuterated NMR solvents were purchased from Sigma-Aldrich or Cambridge Isotope Laboratories, and stored over 3 Å molecular sieves for 12 hours before use. Visible absorption spectroscopy was performed on a Shimadzu 2550 spectrometer. X-Ray crystal structure determinations were performed using a Bruker Kappa APEX II DUO diffractometer equipped with an Oxford Cryostream. $[Mn^{II}_2(\mu\text{-}NHPh)_2(NR_2)_2(THF)_2]$ (**1b**) was prepared according to a previously described protocol.[24] Cyclic voltammagrams were obtained using a CHI-630D electrochemical analyzer/workstation with PIcoamp booster. Electrochemical studies were performed under anaerobic conditions using 7 mg **3** in 5 mL of 1:1 acetonitrile:pyridine solvent with *tert*-butyl ammonium perchlorate electrolyte (0.1 M) using a standard three-electrode assembly; glassy carbon working, Pt wire auxiliary, and a $Ag/AgClO_4$ (0.01 M) reference were employed. Potentials were corrected to ferrocene, which was used as an internal standard. Microanalysis data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester. Samples were weighed with a PerkinElmer Model AD-6 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

$[Mn_4(\mu\text{-}N_2Ph_2)_2(\mu\text{-}HNPh_2)_4(py)_4]$

Method 1: To a solution of $[Mn[N(Si(CH_3)_3)_2]_2$ (360 mg, 0.9209 mmol) in 3 mL of pyridine was added a solution of aniline (HNPh) (90µL, 0.9874 mmol) in 1 mL of pyridine. The mixture was allowed to react for 10 minutes. Then a solution of *N,N′-diphenylhydrazine* (75 mg, 0.4076 mmol) in 3 mL of toluene and 10 mL of pentane was added. This mixture was agitated for 30 seconds and placed in the freezer at -40° C for 3 hours. An orange/red solid was formed and the solution was decanted. The orange solid was dried in vacuo and dissolved in 3 mL of DCM and 3 mL of pyridine. The solution was gently heated at 35° C until all solid was dissolved and was placed in the freezer at -40° C for 48 hours. The solution was decanted and the red-orange crystals were washed 3-5 times with 3 mL aliquots of pentane and dried in vacuo. The crystals were identified using X-ray crystallography. Yield: 222 mg (0.1543 mmols, 75.8%). Anal. Calcd for $C_{53}H_{66}Mn_4N_{12} \cdot \frac{1}{2}\ CH_2Cl_2$: C, 62.73%; H, 5.00%; N, 12.82%. Found: C, 62.55%, H, 4.91%; N, 12.72%. UV-Vis (dichloromethane): λ_{max} [nm] (ε x 10^{-5}) 240(2.0), 286 (0.66), 332 (0.22).

Method 2 via Addition of Diphenylhydrazine and Heat: To a solution of **2** (75 mg, 0.0499 mmol) in 6 mL of DCM was added a solution of *N, N'-diphenylhydrazine* (10 mg, 0.05435 mmol) in 4 mL of DCM. The mixture was stirred and heated at 45° C for 2 hours in a pressure flask. The solution was allowed to cool to 25° C and then dried in

vacuo. The solid was washed 3 times with 5 mL of pentane and extracted 3 times with 3 mL of toluene to remove unreacted **2** and hydrazine. The resulting residue (crude **3**) was dissolved in 1 mL of pyridine. Red crystals were isolated through a pyridine/ether vapor diffusion in a double-vial apparatus. The crystals were washed 3-5 times with 3 mL aliquots of pentane and dried in vacuo. The crystals were isomorphic and identified by X-ray crystallography as the orthorhombic F tetrapyridine solvate polymorph: a = 18.1979(16) Å, b = 22.599(2) Å, c = 40.496(5) Å, α = 90°, β = 90°, γ = 90°. Yield: 10 mg, 0.00782 mmol (15.8% yield).

Quantification of azobenzene: 0.06165 mmol of azobenzene (slightly more than one equivalent per hydrazine added) was quantified in the pentane extract of the above reaction (method 2) using ^{1}H-NMR. The pentane extraction from above was dried in vacuo. The solid was dissolved in C_6D_6 and analyzed with 2 μL of THF as an internal standard.

Control experiment for the conversion of 2 to 3 with diphenylhydrazine: 2 was heated at 45°C for 2 hours *without* the addition of hydrazine. While some azobenzene was observed due to thermal decomposition, the appearance of the final pyridine extract was different (dark reddish black), and crystals of **3** could not be obtained from this extract.

Cyclic Voltammetry

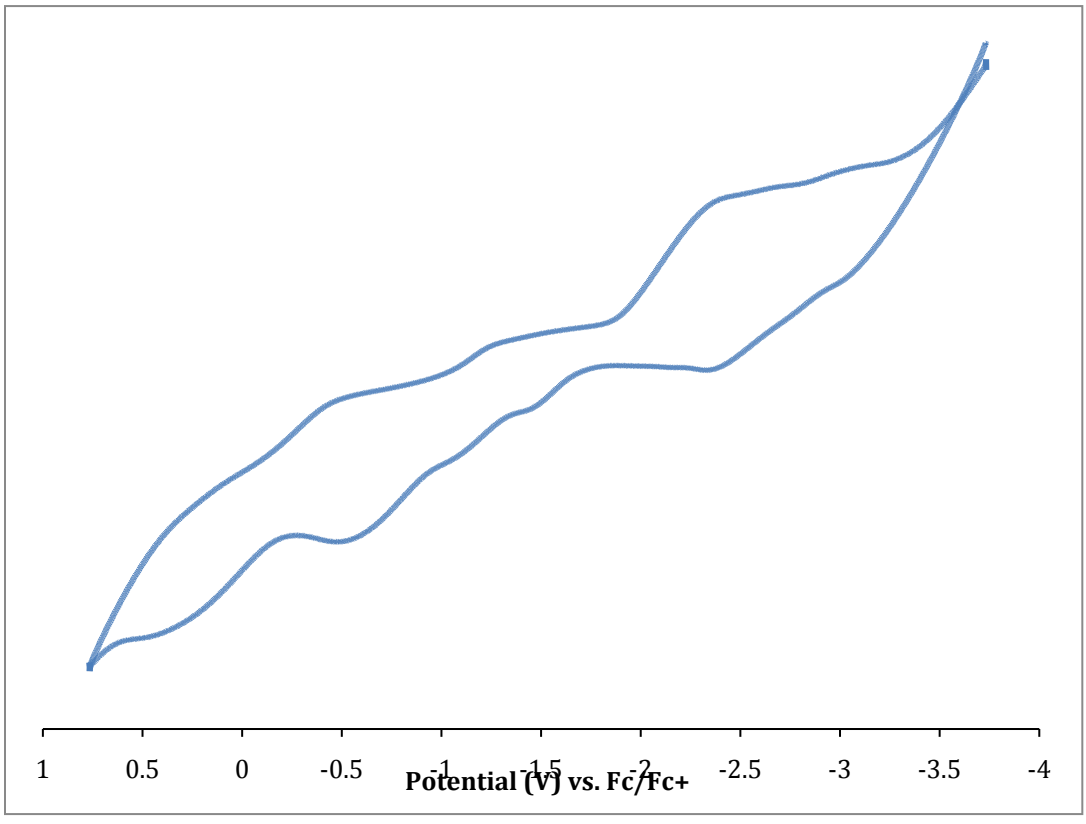

Figure S1. Cyclic voltammagram of **3** vs. ferrocene. Scan rate 100 mV/s, OCP = -1.63 V.

Crystal Structure Report for 3

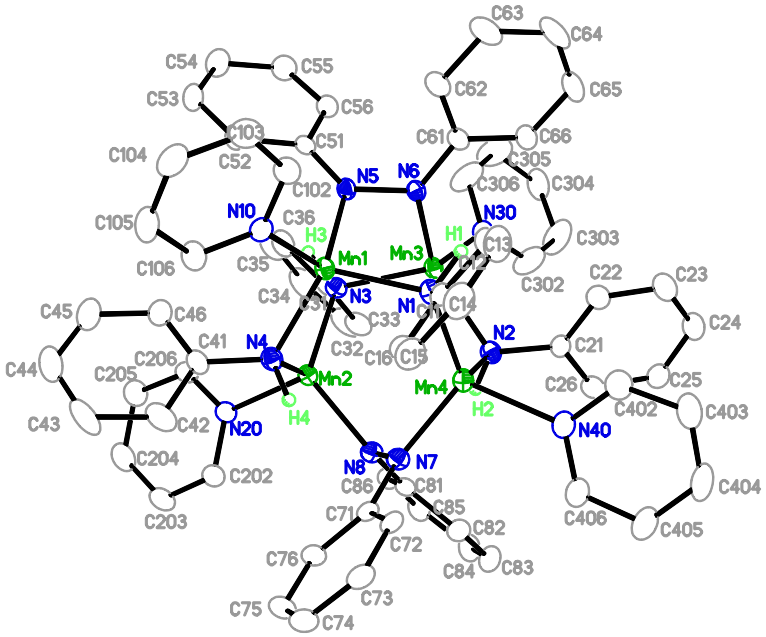

Figure X1. Structure of **3**·4 CH_2Cl_2. Ellipsoids set at 30% probability level. C-H hydrogens omitted for clarity. N-H hydrogens shown as open circles.

A specimen of $C_{73}H_{69}Mn_4N_{13}$, approximate dimensions 0.370 mm x 0.420 mm x 0.430 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 62461 reflections to a maximum θ angle of 27.99° (0.76 Å resolution), of which 15944 were independent (average redundancy 3.918, completeness = 99.5%, R_{int} = 3.29%) and 13424 (84.19%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.6312(10) Å, b = 18.1096(13) Å, c = 27.002(2) Å, β = 93.5179(15)°, volume = 6653.0(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6859 and 0.7456.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{73}H_{69}Mn_4N_{13}$. The final anisotropic full-matrix least-squares refinement on F^2 with 811 variables converged at R1 = 4.43%, for the observed data and wR2 = 10.27% for all data. The goodness-of-fit was 1.111. The largest peak in the final difference electron density synthesis was 0.781 $e^-/Å^3$ and the largest hole was -0.443 $e^-/Å^3$ with an RMS deviation of 0.061 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.346 g/cm^3 and F(000), 2792 e^-.

Table X1.1. Sample and crystal data for 3.

Chemical formula	$C_{73}H_{69}Mn_4N_{13}$	
Formula weight	1348.17	
Temperature	101(2) K	
Wavelength	0.71073 Å	
Crystal size	0.370 x 0.420 x 0.430 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.6312(10) Å	α = 90°
	b = 18.1096(13) Å	β = 93.5179(15)°
	c = 27.002(2) Å	γ = 90°
Volume	6653.0(8) $Å^3$	
Z	4	
Density (calculated)	1.346 g/cm^3	
Absorption coefficient	0.795 mm^{-1}	
F(000)	2792	

Table X1.2. Data collection and structure refinement for 3.

Theta range for data collection	1.36 to 27.99°	
Index ranges	-18<=h<=14, -19<=k<=23, -35<=l<=35	
Reflections collected	62461	
Independent reflections	15944 [R(int) = 0.0329]	
Max. and min. transmission	0.7456 and 0.6859	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	15944 / 0 / 811	
Goodness-of-fit on F^2	1.111	
Δ/σ_{max}	0.001	
Final R indices	13424 data; I>2σ(I)	R1 = 0.0443, wR2 = 0.0957
	all data	R1 = 0.0564, wR2 = 0.1027
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0185P)^2+9.6585P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.781 and -0.443 eÅ^{-3}	
R.M.S. deviation from mean	0.061 eÅ^{-3}	

Table X1.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mn1	0.21091(2)	0.16357(2)	0.20890(2)	0.02384(8)
Mn2	0.26369(2)	0.18696(2)	0.08740(2)	0.02462(8)
Mn3	0.07001(2)	0.28653(2)	0.12015(2)	0.02499(8)
Mn4	0.28531(3)	0.33892(2)	0.18227(2)	0.02680(8)
N10	0.24576(14)	0.08747(11)	0.27107(7)	0.0279(4)
N3	0.10755(14)	0.19111(11)	0.07870(7)	0.0289(4)
N1	0.22589(15)	0.27331(11)	0.23783(7)	0.0295(4)
N4	0.31633(15)	0.14010(11)	0.15634(7)	0.0300(4)
N2	0.17800(15)	0.37180(11)	0.12547(7)	0.0298(4)
N5	0.06389(14)	0.16334(10)	0.18999(7)	0.0257(4)
N8	0.35105(14)	0.27826(11)	0.08884(7)	0.0283(4)
N6	0.02509(14)	0.23730(10)	0.18246(7)	0.0260(4)
N7	0.38923(14)	0.30061(11)	0.13793(7)	0.0288(4)
N30	0.94390(15)	0.33736(11)	0.07877(7)	0.0304(4)
N40	0.33351(16)	0.44557(12)	0.21453(7)	0.0340(5)

	x/a	y/b	z/c	U(eq)
C51	0.00021(16)	0.10784(13)	0.17502(8)	0.0248(4)
C61	0.96652(16)	0.26178(13)	0.21885(8)	0.0268(5)
N20	0.30825(14)	0.11370(11)	0.02817(7)	0.0288(4)
C22	0.0899(2)	0.46184(15)	0.17255(10)	0.0375(6)
C21	0.14151(17)	0.44435(13)	0.13165(9)	0.0297(5)
C23	0.0474(2)	0.53008(17)	0.17748(12)	0.0479(7)
C26	0.1553(2)	0.50012(15)	0.09633(10)	0.0385(6)
C24	0.0561(2)	0.58320(16)	0.14131(12)	0.0476(7)
C25	0.1108(2)	0.56936(15)	0.10110(12)	0.0433(6)
C66	0.92524(17)	0.33353(14)	0.21453(10)	0.0334(5)
C65	0.86731(19)	0.36183(17)	0.25017(11)	0.0425(7)
C64	0.8458(2)	0.3205(2)	0.29092(11)	0.0520(8)
C62	0.94273(19)	0.21994(16)	0.26030(9)	0.0357(6)
C63	0.8827(2)	0.2494(2)	0.29539(10)	0.0487(7)
C86	0.31595(18)	0.31563(14)	0.00433(9)	0.0314(5)
C81	0.35848(16)	0.33032(13)	0.05268(9)	0.0286(5)
C85	0.3177(2)	0.36678(16)	0.96670(10)	0.0400(6)
C82	0.4047(2)	0.39943(15)	0.05961(10)	0.0382(6)
C83	0.4042(2)	0.45040(16)	0.02113(11)	0.0472(7)
C84	0.3618(2)	0.43503(16)	0.97449(11)	0.0475(7)
C71	0.48552(17)	0.28208(13)	0.14978(9)	0.0289(5)
C72	0.52662(18)	0.30157(13)	0.19744(9)	0.0310(5)
C76	0.54712(18)	0.24343(15)	0.11880(10)	0.0368(6)
C73	0.62237(19)	0.28307(15)	0.21281(11)	0.0389(6)
C74	0.68141(19)	0.24386(17)	0.18204(12)	0.0455(7)
C75	0.6427(2)	0.22459(17)	0.13543(12)	0.0457(7)
C202	0.39606(19)	0.12147(15)	0.00905(9)	0.0352(5)
C206	0.25136(19)	0.05756(15)	0.01149(9)	0.0354(5)
C204	0.3710(2)	0.01615(18)	0.95746(10)	0.0481(7)
C205	0.2798(2)	0.00750(17)	0.97659(11)	0.0450(7)
C203	0.4295(2)	0.07393(17)	0.97374(10)	0.0443(7)
C31	0.06255(16)	0.18333(14)	0.03043(9)	0.0306(5)
C34	0.9781(3)	0.1640(3)	0.93438(13)	0.0697(12)
C36	0.0032(2)	0.12101(18)	0.01812(12)	0.0491(7)
C33	0.0327(3)	0.2264(2)	0.94636(11)	0.0632(10)
C32	0.0740(2)	0.23535(18)	0.99399(10)	0.0447(7)
C35	0.9623(2)	0.1115(2)	0.96963(14)	0.0627(10)
C304	0.7792(2)	0.39722(17)	0.02864(10)	0.0478(8)
C302	0.9450(2)	0.40305(19)	0.05732(12)	0.0579(9)
C305	0.7744(2)	0.3316(2)	0.05188(15)	0.0694(11)
C303	0.8640(3)	0.43447(19)	0.03250(13)	0.0665(11)

	x/a	y/b	z/c	U(eq)
C306	0.8587(2)	0.30323(19)	0.07602(14)	0.0653(11)
C52	0.03055(18)	0.03341(13)	0.18109(9)	0.0301(5)
C56	0.90438(18)	0.11942(14)	0.15355(9)	0.0311(5)
C55	0.8460(2)	0.06074(16)	0.13759(10)	0.0402(6)
C53	0.9704(2)	0.97554(14)	0.16529(10)	0.0394(6)
C54	0.8779(2)	0.98823(16)	0.14270(11)	0.0452(7)
C41	0.34796(19)	0.06601(14)	0.14975(8)	0.0315(5)
C46	0.2806(2)	0.01192(15)	0.13528(10)	0.0423(6)
C42	0.4478(2)	0.0469(2)	0.15773(11)	0.0511(8)
C44	0.4051(4)	0.9195(2)	0.13831(15)	0.0755(13)
C43	0.4756(3)	0.9719(2)	0.15246(14)	0.0721(13)
C45	0.3095(3)	0.93985(18)	0.12915(13)	0.0630(10)
C402	0.2837(2)	0.48286(18)	0.24708(11)	0.0491(7)
C403	0.2994(3)	0.5567(2)	0.25727(14)	0.0677(10)
C406	0.4037(2)	0.48216(15)	0.19211(10)	0.0415(6)
C405	0.4250(3)	0.55581(16)	0.20055(11)	0.0520(8)
C11	0.27325(17)	0.27579(12)	0.28619(8)	0.0254(4)
C16	0.36961(19)	0.25247(14)	0.29381(10)	0.0344(5)
C14	0.3679(2)	0.27906(16)	0.38066(10)	0.0463(7)
C15	0.4170(2)	0.25408(16)	0.34055(10)	0.0426(6)
C12	0.2236(2)	0.30035(15)	0.32730(10)	0.0380(6)
C13	0.2718(2)	0.30165(16)	0.37444(10)	0.0458(7)
C102	0.1951(2)	0.09409(15)	0.31161(9)	0.0381(6)
C104	0.2693(2)	0.98733(16)	0.34878(10)	0.0457(7)
C106	0.3093(2)	0.03139(15)	0.26985(9)	0.0376(6)
C105	0.3233(2)	0.98058(15)	0.30769(10)	0.0447(7)
C103	0.2049(2)	0.04557(18)	0.35123(10)	0.0479(7)
C4A	0.6788(2)	0.3145(2)	0.90743(14)	0.0563(8)
N1A	0.6113(3)	0.2244(2)	0.98163(13)	0.0751(10)
C5A	0.5969(2)	0.3327(2)	0.93096(14)	0.0616(10)
C6A	0.5664(2)	0.2866(3)	0.96765(14)	0.0706(12)
C2A	0.6926(4)	0.2092(2)	0.95850(17)	0.0834(14)
C404	0.3716(3)	0.59346(18)	0.23370(13)	0.0625(9)
C3A	0.7281(3)	0.2521(2)	0.92199(15)	0.0701(11)

Table X1.4. Bond lengths (Å) for 3.

Mn1-N5	2.0376(19)	Mn1-N4	2.124(2)
Mn1-N1	2.140(2)	Mn1-N10	2.2013(19)
Mn2-N8	2.036(2)	Mn2-N3	2.1283(19)
Mn2-N4	2.130(2)	Mn2-N20	2.192(2)

Mn3-N6	2.0315(19)	Mn3-N2	2.132(2)
Mn3-N3	2.138(2)	Mn3-N30	2.1944(19)
Mn4-N7	2.032(2)	Mn4-N1	2.114(2)
Mn4-N2	2.1381(19)	Mn4-N40	2.202(2)
N10-C102	1.335(3)	N10-C106	1.337(3)
N3-C31	1.413(3)	N1-C11	1.421(3)
N4-C41	1.424(3)	N2-C21	1.418(3)
N5-C51	1.373(3)	N5-N6	1.450(3)
N8-C81	1.366(3)	N8-N7	1.451(3)
N6-C61	1.377(3)	N7-C71	1.373(3)
N30-C306	1.314(4)	N30-C302	1.324(4)
N40-C402	1.327(4)	N40-C406	1.339(4)
C51-C56	1.412(3)	C51-C52	1.416(3)
C61-C62	1.406(3)	C61-C66	1.418(3)
N20-C206	1.340(3)	N20-C202	1.340(3)
C22-C23	1.374(4)	C22-C21	1.382(4)
C21-C26	1.409(4)	C23-C24	1.381(4)
C26-C25	1.402(4)	C24-C25	1.377(4)
C66-C65	1.381(4)	C65-C64	1.377(5)
C64-C63	1.384(5)	C62-C63	1.395(4)
C86-C85	1.376(4)	C86-C81	1.421(3)
C81-C82	1.408(3)	C85-C84	1.385(4)

Table X1.4 (cont)

C82-C83	1.390(4)	C83-C84	1.381(4)
C71-C76	1.407(4)	C71-C72	1.416(3)
C72-C73	1.386(3)	C76-C75	1.394(4)
C73-C74	1.387(4)	C74-C75	1.380(4)
C202-C203	1.383(4)	C206-C205	1.380(4)
C204-C203	1.372(4)	C204-C205	1.384(4)
C31-C32	1.378(4)	C31-C36	1.416(4)
C34-C35	1.372(6)	C34-C33	1.380(6)
C36-C35	1.402(4)	C33-C32	1.382(4)
C304-C303	1.336(5)	C304-C305	1.348(5)
C302-C303	1.379(4)	C305-C306	1.384(4)
C52-C53	1.382(4)	C56-C55	1.381(4)
C55-C54	1.387(4)	C53-C54	1.386(4)
C41-C46	1.383(4)	C41-C42	1.409(4)
C46-C45	1.376(4)	C42-C43	1.420(5)
C44-C45	1.363(6)	C44-C43	1.386(6)
C402-C403	1.380(4)	C403-C404	1.375(5)
C406-C405	1.381(4)	C405-C404	1.370(5)
C11-C16	1.383(3)	C11-C12	1.407(3)

C16-C15	1.382(4)	C14-C13	1.373(4)
C14-C15	1.383(4)	C12-C13	1.396(4)
C102-C103	1.385(4)	C104-C105	1.374(4)
C104-C103	1.377(4)	C106-C105	1.379(4)
C4A-C5A	1.359(5)	C4A-C3A	1.360(5)
N1A-C6A	1.325(6)	N1A-C2A	1.333(5)
C5A-C6A	1.380(6)	C2A-C3A	1.367(5)

Table X1.5. Bond angles (°) for 3.

N5-Mn1-N4	121.84(8)	N5-Mn1-N1	99.43(8)
N4-Mn1-N1	112.11(8)	N5-Mn1-N10	110.66(7)
N4-Mn1-N10	105.13(8)	N1-Mn1-N10	106.96(7)
N8-Mn2-N3	123.58(8)	N8-Mn2-N4	98.14(8)
N3-Mn2-N4	113.05(8)	N8-Mn2-N20	108.51(8)
N3-Mn2-N20	105.12(7)	N4-Mn2-N20	107.63(7)
N6-Mn3-N2	120.27(8)	N6-Mn3-N3	99.95(8)
N2-Mn3-N3	115.74(8)	N6-Mn3-N30	109.83(8)
N2-Mn3-N30	104.27(8)	N3-Mn3-N30	106.12(7)
N7-Mn4-N1	122.52(8)	N7-Mn4-N2	98.24(8)
N1-Mn4-N2	112.99(8)	N7-Mn4-N40	109.31(8)
N1-Mn4-N40	109.28(8)	N2-Mn4-N40	102.35(8)
C102-N10-C106	117.2(2)	C102-N10-Mn1	118.09(17)
C106-N10-Mn1	124.53(17)	C31-N3-Mn2	118.22(15)
C31-N3-Mn3	117.34(15)	Mn2-N3-Mn3	103.92(8)
C11-N1-Mn4	117.52(15)	C11-N1-Mn1	113.10(14)
Mn4-N1-Mn1	107.15(8)	C41-N4-Mn1	119.65(15)
C41-N4-Mn2	110.77(14)	Mn1-N4-Mn2	107.38(9)
C21-N2-Mn3	115.67(15)	C21-N2-Mn4	113.76(15)
Mn3-N2-Mn4	106.60(9)	C51-N5-N6	114.62(17)
C51-N5-Mn1	132.05(15)	N6-N5-Mn1	112.20(13)
C81-N8-N7	114.97(19)	C81-N8-Mn2	128.01(15)
N7-N8-Mn2	114.86(14)	C61-N6-N5	114.84(18)
C61-N6-Mn3	131.85(16)	N5-N6-Mn3	113.30(13)
C71-N7-N8	115.38(19)	C71-N7-Mn4	129.56(16)
N8-N7-Mn4	114.17(13)	C306-N30-C302	115.6(2)
C306-N30-Mn3	119.58(18)	C302-N30-Mn3	124.77(19)
C402-N40-C406	117.1(2)	C402-N40-Mn4	123.8(2)
C406-N40-Mn4	117.34(17)	N5-C51-C56	124.4(2)
N5-C51-C52	119.2(2)	C56-C51-C52	116.4(2)
N6-C61-C62	124.5(2)	N6-C61-C66	118.7(2)
C62-C61-C66	116.7(2)	C206-N20-C202	117.6(2)
C206-N20-Mn2	121.60(16)	C202-N20-Mn2	120.76(17)
C23-C22-C21	121.4(3)	C22-C21-C26	118.2(2)
C22-C21-N2	120.4(2)	C26-C21-N2	121.5(2)
C22-C23-C24	120.2(3)	C25-C26-C21	120.2(2)

Table X1.5 (cont)

C25-C24-C23	120.3(3)	C24-C25-C26	119.5(3)
C65-C66-C61	121.6(3)	C64-C65-C66	120.9(3)
C65-C64-C63	118.8(3)	C63-C62-C61	120.5(3)
C64-C63-C62	121.5(3)	C85-C86-C81	121.9(2)

N8-C81-C82	124.8(2)	N8-C81-C86	118.9(2)
C82-C81-C86	116.3(2)	C86-C85-C84	121.0(3)
C83-C82-C81	120.6(3)	C84-C83-C82	122.0(3)
C83-C84-C85	118.1(3)	N7-C71-C76	125.4(2)
N7-C71-C72	118.0(2)	C76-C71-C72	116.5(2)
C73-C72-C71	121.6(2)	C75-C76-C71	120.7(3)
C72-C73-C74	121.0(3)	C75-C74-C73	118.2(2)
C74-C75-C76	122.0(3)	N20-C202-C203	122.7(3)
N20-C206-C205	123.2(2)	C203-C204-C205	119.0(3)
C206-C205-C204	118.5(3)	C204-C203-C202	119.1(3)
C32-C31-N3	121.9(2)	C32-C31-C36	117.7(3)
N3-C31-C36	120.4(2)	C35-C34-C33	120.7(3)
C35-C36-C31	120.4(3)	C34-C33-C32	119.8(4)
C31-C32-C33	121.8(3)	C34-C35-C36	119.4(3)
C303-C304-C305	118.4(3)	N30-C302-C303	123.6(3)
C304-C305-C306	118.9(3)	C304-C303-C302	119.5(3)
N30-C306-C305	123.9(3)	C53-C52-C51	121.5(2)
C55-C56-C51	121.0(2)	C56-C55-C54	121.8(2)
C52-C53-C54	121.1(2)	C53-C54-C55	118.2(2)
C46-C41-C42	119.2(3)	C46-C41-N4	120.1(2)
C42-C41-N4	120.7(3)	C45-C46-C41	121.0(3)
C41-C42-C43	118.8(4)	C45-C44-C43	120.3(3)
C44-C43-C42	119.8(3)	C44-C45-C46	120.8(4)
N40-C402-C403	123.1(3)	C404-C403-C402	118.9(3)
N40-C406-C405	123.5(3)	C404-C405-C406	118.2(3)
C16-C11-C12	118.5(2)	C16-C11-N1	120.0(2)
C12-C11-N1	121.4(2)	C15-C16-C11	121.0(3)
C13-C14-C15	120.3(3)	C16-C15-C14	120.0(3)
C13-C12-C11	120.1(3)	C14-C13-C12	119.9(3)
N10-C102-C103	123.1(3)	C105-C104-C103	118.8(3)
N10-C106-C105	123.3(3)	C104-C105-C106	118.9(3)
C104-C103-C102	118.7(3)	C5A-C4A-C3A	118.2(4)
C6A-N1A-C2A	115.1(4)	C4A-C5A-C6A	118.7(4)

Table X1.5 (cont)

N1A-C6A-C5A	124.4(3)	N1A-C2A-C3A	124.2(4)
C405-C404-C403	119.1(3)	C4A-C3A-C2A	119.4(3)

Table X1.6. Torsion angles (°) for 3.

C51-N5-N6-C61	82.1(2)	Mn1-N5-N6-C61	-108.48(17)
C51-N5-N6-Mn3	-98.96(18)	Mn1-N5-N6-Mn3	70.44(15)
C81-N8-N7-C71	-93.0(2)	Mn2-N8-N7-C71	102.35(19)

C81-N8-N7-Mn4	96.79(19)	Mn2-N8-N7-Mn4	-67.89(17)
N6-N5-C51-C56	0.4(3)	Mn1-N5-C51-C56	-166.30(17)
N6-N5-C51-C52	-179.50(19)	Mn1-N5-C51-C52	13.8(3)
N5-N6-C61-C62	-1.0(3)	Mn3-N6-C61-C62	-179.69(18)
N5-N6-C61-C66	-179.93(18)	Mn3-N6-C61-C66	1.4(3)
C23-C22-C21-C26	4.1(4)	C23-C22-C21-N2	-175.0(2)
Mn3-N2-C21-C22	60.5(3)	Mn4-N2-C21-C22	-63.4(3)
Mn3-N2-C21-C26	-118.5(2)	Mn4-N2-C21-C26	117.6(2)
C21-C22-C23-C24	-0.3(5)	C22-C21-C26-C25	-4.9(4)
N2-C21-C26-C25	174.2(2)	C22-C23-C24-C25	-2.8(5)
C23-C24-C25-C26	1.9(5)	C21-C26-C25-C24	2.0(4)
N6-C61-C66-C65	-178.8(2)	C62-C61-C66-C65	2.2(3)
C61-C66-C65-C64	-1.4(4)	C66-C65-C64-C63	-0.5(4)
N6-C61-C62-C63	179.9(2)	C66-C61-C62-C63	-1.1(4)
C65-C64-C63-C62	1.6(4)	C61-C62-C63-C64	-0.7(4)
N7-N8-C81-C82	4.0(3)	Mn2-N8-C81-C82	166.33(19)
N7-N8-C81-C86	-174.99(19)	Mn2-N8-C81-C86	-12.7(3)
C85-C86-C81-N8	177.6(2)	C85-C86-C81-C82	-1.5(3)
C81-C86-C85-C84	0.4(4)	N8-C81-C82-C83	-176.7(2)
C86-C81-C82-C83	2.3(4)	C81-C82-C83-C84	-2.1(4)
C82-C83-C84-C85	0.8(5)	C86-C85-C84-C83	0.0(4)
N8-N7-C71-C76	-0.8(3)	Mn4-N7-C71-C76	167.63(19)
N8-N7-C71-C72	-179.20(19)	Mn4-N7-C71-C72	-10.8(3)
N7-C71-C72-C73	178.2(2)	C76-C71-C72-C73	-0.4(3)
N7-C71-C76-C75	-177.1(2)	C72-C71-C76-C75	1.3(4)
C71-C72-C73-C74	-0.7(4)	C72-C73-C74-C75	0.8(4)
C73-C74-C75-C76	0.1(4)	C71-C76-C75-C74	-1.2(4)
C206-N20-C202-C203	-0.6(4)	Mn2-N20-C202-C203	176.2(2)

Table X1.6 (cont)

C202-N20-C206-C205	1.1(4)	Mn2-N20-C206-C205	-175.7(2)
N20-C206-C205-C204	-0.8(4)	C203-C204-C205-C206	-0.1(5)
C205-C204-C203-C202	0.5(4)	N20-C202-C203-C204	-0.1(4)
Mn2-N3-C31-C32	-66.1(3)	Mn3-N3-C31-C32	59.7(3)
Mn2-N3-C31-C36	114.2(2)	Mn3-N3-C31-C36	-120.0(2)
C32-C31-C36-C35	3.3(4)	N3-C31-C36-C35	-177.0(3)
C35-C34-C33-C32	1.5(5)	N3-C31-C32-C33	177.7(3)
C36-C31-C32-C33	-2.5(4)	C34-C33-C32-C31	0.2(5)
C33-C34-C35-C36	-0.8(5)	C31-C36-C35-C34	-1.6(5)
C306-N30-C302-C303	-1.4(5)	Mn3-N30-C302-C303	-178.4(3)
C303-C304-C305-C306	-4.1(6)	C305-C304-C303-C302	3.9(6)
N30-C302-C303-C304	-1.2(6)	C302-N30-C306-C305	1.2(6)
Mn3-N30-C306-C305	178.4(3)	C304-C305-C306-N30	1.6(7)

N5-C51-C52-C53	-178.0(2)	C56-C51-C52-C53	2.0(3)
N5-C51-C56-C55	177.4(2)	C52-C51-C56-C55	-2.7(3)
C51-C56-C55-C54	1.2(4)	C51-C52-C53-C54	0.2(4)
C52-C53-C54-C55	-1.8(4)	C56-C55-C54-C53	1.1(4)
Mn1-N4-C41-C46	59.4(3)	Mn2-N4-C41-C46	-66.3(2)
Mn1-N4-C41-C42	-120.7(2)	Mn2-N4-C41-C42	113.6(2)
C42-C41-C46-C45	0.8(4)	N4-C41-C46-C45	-179.4(2)
C46-C41-C42-C43	-2.4(4)	N4-C41-C42-C43	177.8(2)
C45-C44-C43-C42	0.4(5)	C41-C42-C43-C44	1.8(5)
C43-C44-C45-C46	-2.1(5)	C41-C46-C45-C44	1.5(5)
C406-N40-C402-C403	1.9(5)	Mn4-N40-C402-C403	-162.6(3)
N40-C402-C403-C404	-1.7(6)	C402-N40-C406-C405	-1.1(4)
Mn4-N40-C406-C405	164.4(2)	N40-C406-C405-C404	0.0(5)
Mn4-N1-C11-C16	-62.4(3)	Mn1-N1-C11-C16	63.3(2)
Mn4-N1-C11-C12	118.9(2)	Mn1-N1-C11-C12	-115.4(2)
C12-C11-C16-C15	-0.9(4)	N1-C11-C16-C15	-179.7(2)
C11-C16-C15-C14	0.2(4)	C13-C14-C15-C16	0.7(4)
C16-C11-C12-C13	0.7(4)	N1-C11-C12-C13	179.5(2)
C15-C14-C13-C12	-0.8(4)	C11-C12-C13-C14	0.1(4)
C106-N10-C102-C103	-0.8(4)	Mn1-N10-C102-C103	174.5(2)
C102-N10-C106-C105	0.9(4)	Mn1-N10-C106-C105	-174.0(2)
C103-C104-C105-C106	-1.5(4)	N10-C106-C105-C104	0.2(5)
C105-C104-C103-C102	1.6(5)	N10-C102-C103-C104	-0.5(5)
C3A-C4A-C5A-C6A	-1.3(5)	C2A-N1A-C6A-C5A	1.9(6)

Table X1.6 (cont)

C4A-C5A-C6A-N1A	-0.6(5)	C6A-N1A-C2A-C3A	-1.6(7)
C406-C405-C404-C403	0.2(5)	C402-C403-C404-C405	0.5(6)
C5A-C4A-C3A-C2A	1.7(6)	N1A-C2A-C3A-C4A	-0.2(7)

Crystal Structure Report for 3_DCM

A specimen of $C_{72}H_{72}Cl_8Mn_4N_{12}$, approximate dimensions 0.080 mm x 0.120 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a tetragonal unit cell yielded a total of 24305 reflections to a maximum θ angle of 26.67° (0.79 Å resolution), of which 4129 were independent (average redundancy 5.886, completeness = 99.0%, R_{int} = 4.01%) and 3268 (79.15%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.311(4) Å, b = 18.311(4) Å, c = 47.150(11) Å, volume = 15809.(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5503 and 0.7454.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group I 41/a c d, with Z = 8 for the formula unit, $C_{72}H_{72}Cl_8Mn_4N_{12}$. The final anisotropic full-matrix least-squares refinement on F^2 with 273 variables converged at R1 = 4.71%, for the observed data and wR2 = 13.10% for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 0.490 $e^-/Å^3$ and the largest hole was -0.553 $e^-/Å^3$ with an RMS deviation of 0.057 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.352 g/cm^3 and F(000), 6592 e^-.

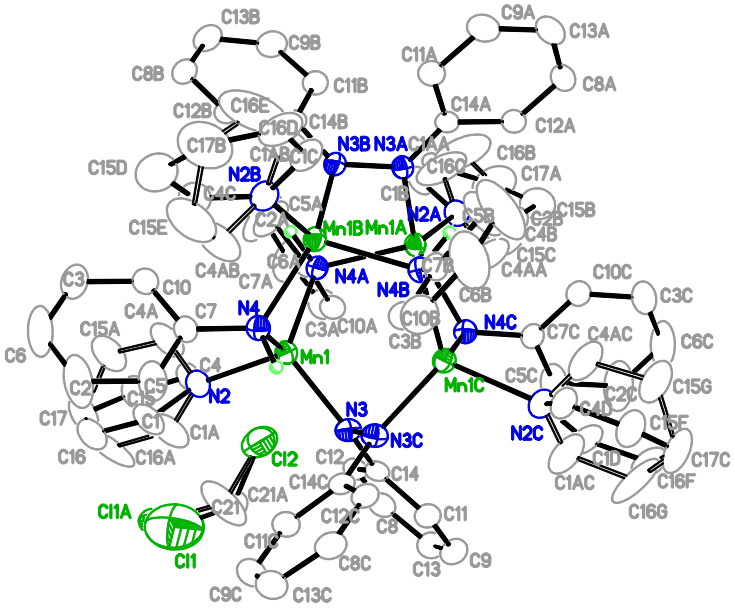

Figure X2. Structure of **3**·4 CH_2Cl_2. Ellipsoids set at 30% probability level. C-H hydrogens omitted for clarity. N-H hydrogens shown as open circles.

Table X2.1. Sample and crystal data for 3_DCM.

Chemical formula	$C_{72}H_{72}Cl_8Mn_4N_{12}$	
Formula weight	1608.77	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.120 x 0.140 mm	
Crystal system	tetragonal	
Space group	I 41/a c d	
Unit cell dimensions	a = 18.311(4) Å	α = 90°
	b = 18.311(4) Å	β = 90°
	c = 47.150(11) Å	γ = 90°
Volume	15809.(8) $Å^3$	
Z	8	
Density (calculated)	1.352 g/cm^3	
Absorption coefficient	0.942 mm^{-1}	
F(000)	6592	

Table X2.2. Data collection and structure refinement for 3_DCM.

Theta range for data collection	2.39 to 26.67°	
Index ranges	-22<=h<=22, -22<=k<=22, -59<=l<=49	
Reflections collected	24305	
Independent reflections	4129 [R(int) = 0.0401]	
Max. and min. transmission	0.7454 and 0.5503	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4129 / 0 / 273	
Goodness-of-fit on F^2	1.048	
Δ/σ_{max}	0.002	
Final R indices	3268 data; I>2σ(I)	R1 = 0.0471, wR2 = 0.1138
	all data	R1 = 0.0647, wR2 = 0.1310
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0494P)^2+41.9246P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.490 and -0.553 eÅ^{-3}	
R.M.S. deviation from mean	0.057 eÅ^{-3}	

Table X2.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3_DCM.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mn1	0.57842(2)	0.31514(2)	0.10082(2)	0.03475(14)
N4	0.48160(12)	0.37446(12)	0.11207(5)	0.0365(5)
N3	0.53947(11)	0.25237(13)	0.06853(4)	0.0381(5)
C14	0.57289(14)	0.20631(15)	0.04971(5)	0.0372(6)
N2	0.65675(13)	0.39595(13)	0.08525(6)	0.0473(6)
C12	0.65052(15)	0.20737(16)	0.04788(6)	0.0404(6)
C11	0.53627(17)	0.15742(16)	0.03161(6)	0.0459(7)
C10	0.53578(16)	0.48625(16)	0.13000(6)	0.0472(7)
C9	0.5753(2)	0.11051(19)	0.01399(7)	0.0580(8)
C8	0.68750(17)	0.16083(17)	0.03010(6)	0.0486(7)
C7	0.49143(14)	0.45110(14)	0.11084(6)	0.0385(6)
C13	0.65055(19)	0.11127(18)	0.01313(7)	0.0564(8)
C6	0.5125(3)	0.6017(2)	0.10850(12)	0.0984(17)
C5	0.4580(2)	0.4925(2)	0.09002(10)	0.0835(13)
C3	0.5460(2)	0.56103(19)	0.12898(9)	0.0657(9)

	x/a	y/b	z/c	U(eq)
C2	0.4692(3)	0.5682(2)	0.08924(14)	0.126(2)
C17	0.7468(4)	0.5091(3)	0.06920(13)	0.113(2)
C15	0.7777(5)	0.4421(6)	0.0787(2)	0.080(3)
C4	0.7271(4)	0.3907(4)	0.0872(2)	0.055(2)
C1	0.6320(7)	0.4573(6)	0.0700(3)	0.063(3)
C16	0.6744(10)	0.5126(7)	0.0622(3)	0.077(4)
C1A	0.6483(10)	0.4290(12)	0.0647(4)	0.126(8)
C16A	0.6948(15)	0.4877(15)	0.0554(4)	0.182(12)
C4A	0.7090(7)	0.4212(8)	0.1036(3)	0.096(5)
C15A	0.7510(7)	0.4805(8)	0.0965(3)	0.108(6)
Cl2	0.87224(14)	0.26260(11)	0.05310(3)	0.1673(10)
C21	0.8945(8)	0.2889(4)	0.02102(16)	0.107(4)
Cl1	0.8552(6)	0.3724(7)	0.01301(13)	0.217(3)
C21A	0.836(2)	0.316(3)	0.0250(8)	0.19(3)
Cl1A	0.8737(5)	0.3928(4)	0.01443(13)	0.080(3)

Table X2.4. Bond lengths (Å) for 3_DCM.

Mn1-N3	2.037(2)	Mn1-N4	2.122(2)
Mn1-N4	2.146(2)	Mn1-N2	2.188(2)
N4-C7	1.416(3)	N4-Mn1	2.122(2)
N3-C14	1.369(3)	N3-N3	1.448(4)
C14-C11	1.407(4)	C14-C12	1.424(4)
N2-C1A	1.155(15)	N2-C4	1.295(8)
N2-C4A	1.371(11)	N2-C1	1.409(12)
C12-C8	1.374(4)	C11-C9	1.392(4)
C10-C7	1.375(4)	C10-C3	1.383(5)
C9-C13	1.379(5)	C8-C13	1.386(5)
C7-C5	1.384(4)	C6-C2	1.353(7)
C6-C3	1.364(6)	C5-C2	1.401(6)
C17-C16A	1.22(2)	C17-C16	1.37(2)
C17-C15A	1.394(12)	C17-C15	1.424(12)
C15-C4	1.379(10)	C1-C16	1.33(2)
C1A-C16A	1.44(2)	C4A-C15A	1.372(12)
Cl2-C21	1.639(7)	Cl2-C21A	1.78(3)
C21-Cl1	1.731(11)	C21A-Cl1A	1.65(2)

Table X2.5. Bond angles (°) for 3_DCM.

N3-Mn1-N4	121.86(9)	N3-Mn1-N4	100.44(8)
N4-Mn1-N4	109.17(7)	N3-Mn1-N2	111.13(9)
N4-Mn1-N2	106.79(9)	N4-Mn1-N2	106.39(9)
C7-N4-Mn1	118.60(17)	C7-N4-Mn1	112.74(17)
Mn1-N4-Mn1	109.63(9)	C14-N3-N3	114.2(2)
C14-N3-Mn1	132.52(17)	N3-N3-Mn1	112.54(14)
N3-C14-C11	124.9(2)	N3-C14-C12	118.5(2)
C11-C14-C12	116.6(3)	C1A-N2-C4A	116.7(8)
C4-N2-C1	114.5(7)	C1A-N2-Mn1	123.3(7)
C4-N2-Mn1	125.4(4)	C4A-N2-Mn1	118.2(4)
C1-N2-Mn1	120.0(6)	C8-C12-C14	121.4(3)
C9-C11-C14	120.7(3)	C7-C10-C3	121.4(3)
C13-C9-C11	121.6(3)	C12-C8-C13	121.2(3)
C10-C7-C5	118.1(3)	C10-C7-N4	120.8(2)
C5-C7-N4	121.1(3)	C9-C13-C8	118.5(3)
C2-C6-C3	119.4(4)	C7-C5-C2	119.7(4)
C6-C3-C10	120.3(4)	C6-C2-C5	121.1(4)
C16A-C17-C15A	114.5(8)	C16-C17-C15	120.2(7)
C4-C15-C17	114.3(8)	N2-C4-C15	126.8(8)
C16-C1-N2	124.2(13)	C1-C16-C17	117.6(12)
N2-C1A-C16A	124.5(14)	C17-C16A-C1A	122.8(13)
N2-C4A-C15A	120.2(8)	C4A-C15A-C17	119.5(9)
Cl2-C21-Cl1	111.0(6)	Cl1A-C21A-Cl2	122.4(13)

Table X2.6. Torsion angles (°) for 3_DCM.

N3-N3-C14-C11	-0.3(4)	Mn1-N3-C14-C11	168.7(2)
N3-N3-C14-C12	179.4(2)	Mn1-N3-C14-C12	-11.6(4)
N3-C14-C12-C8	177.8(3)	C11-C14-C12-C8	-2.5(4)
N3-C14-C11-C9	-177.3(3)	C12-C14-C11-C9	3.0(4)
C14-C11-C9-C13	-1.5(5)	C14-C12-C8-C13	0.3(4)
C3-C10-C7-C5	1.1(5)	C3-C10-C7-N4	179.8(3)
Mn1-N4-C7-C10	61.2(3)	Mn1-N4-C7-C10	-68.8(3)
Mn1-N4-C7-C5	-120.1(3)	Mn1-N4-C7-C5	109.9(3)
C11-C9-C13-C8	-0.7(5)	C12-C8-C13-C9	1.3(5)
C10-C7-C5-C2	-0.8(7)	N4-C7-C5-C2	-179.5(5)
C2-C6-C3-C10	0.1(8)	C7-C10-C3-C6	-0.8(6)
C3-C6-C2-C5	0.2(10)	C7-C5-C2-C6	0.1(10)
C16A-C17-C15-C4	-40.8(15)	C16-C17-C15-C4	-16.3(13)
C15A-C17-C15-C4	71.4(9)	C1A-N2-C4-C15	33.9(14)
C4A-N2-C4-C15	-80.7(11)	C1-N2-C4-C15	7.7(12)
Mn1-N2-C4-C15	-176.8(7)	C17-C15-C4-N2	5.2(13)
C1A-N2-C1-C16	-82.(2)	C4-N2-C1-C16	-11.2(14)
C4A-N2-C1-C16	35.7(14)	Mn1-N2-C1-C16	173.1(9)
N2-C1-C16-C17	0.7(17)	C16A-C17-C16-C1	70.(2)
C15A-C17-C16-C1	-40.1(15)	C15-C17-C16-C1	13.5(16)
C4-N2-C1A-C16A	-37.(2)	C4A-N2-C1A-C16A	9.(3)
C1-N2-C1A-C16A	81.(3)	Mn1-N2-C1A-C16A	173.2(18)
C16-C17-C16A-C1A	-91.(3)	C15A-C17-C16A-C1A	-10.(3)
C15-C17-C16A-C1A	42.(3)	N2-C1A-C16A-C17	-2.(4)
C1A-N2-C4A-C15A	-4.(2)	C4-N2-C4A-C15A	78.3(14)
C1-N2-C4A-C15A	-30.4(16)	Mn1-N2-C4A-C15A	-168.7(11)
N2-C4A-C15A-C17	-8.(2)	C16A-C17-C15A-C4A	14.(2)
C16-C17-C15A-C4A	44.7(18)	C15-C17-C15A-C4A	-70.7(14)
C21A-Cl2-C21-Cl1	29.1(15)	C21-Cl2-C21A-Cl1A	-65.(3)

Crystal Structure Report for 3_Py4

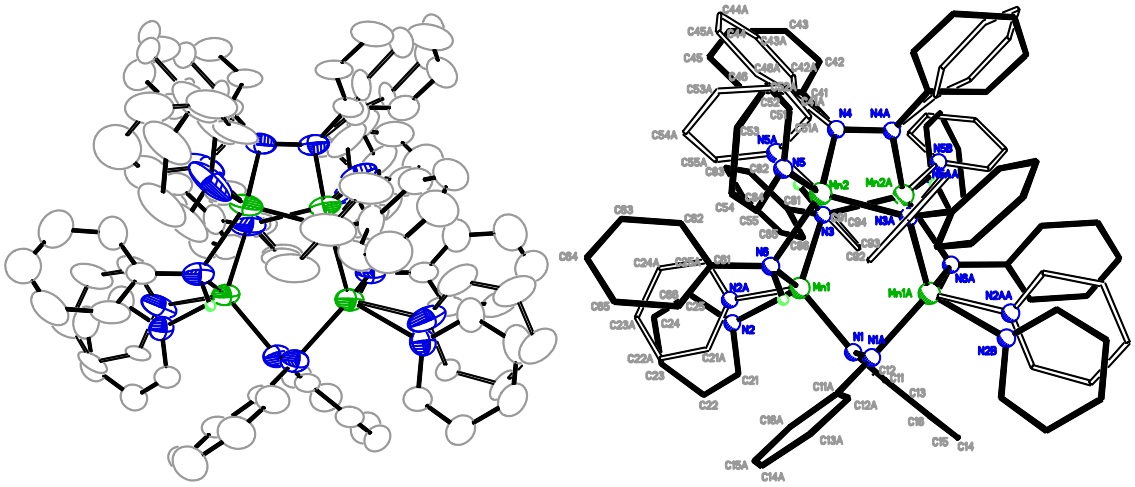

Figure X3. Structure of **3**·4 Py. Left: Ellipsoids set at 30% probability level. C-H hydrogens omitted for clarity. N-H hydrogens shown as open circles. Right: ball and stick view with atom labels.

A specimen of $C_{88}H_{84}Mn_4N_{16}$, approximate dimensions 0.150 mm x 0.250 mm x 0.330 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using an orthorhombic unit cell yielded a total of 11276 reflections to a maximum θ angle of 20.82° (1.00 Å resolution), of which 3678 were independent (average redundancy 3.066, completeness = 99.8%, R_{int} = 2.46%) and 3182 (86.51%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.1979(16) Å, b = 22.599(2) Å, c = 40.496(5) Å, volume = 16654.(3) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6669 and 0.7446.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group F d d 2, with Z = 8 for the formula unit, $C_{88}H_{84}Mn_4N_{16}$. The final anisotropic full-matrix least-squares refinement on F^2 with 594 variables converged at R1 = 3.79%, for the observed data and wR2 = 10.31% for all data. The goodness-of-fit was 1.052. The largest peak in the final difference electron density synthesis was 0.210 $e^-/Å^3$ and the largest hole was -0.154 $e^-/Å^3$ with an RMS deviation of 0.035 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.265 g/cm^3 and F(000), 6592 e^-.

Table X3.1. Sample and crystal data for 3_Py4.

Chemical formula	$C_{88}H_{84}Mn_4N_{16}$	
Formula weight	1585.47	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.250 x 0.330 mm	
Crystal system	orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 18.1979(16) Å	α = 90°
	b = 22.599(2) Å	β = 90°
	c = 40.496(5) Å	γ = 90°
Volume	16654.(3) $Å^3$	
Z	8	
Density (calculated)	1.265 g/cm^3	
Absorption coefficient	0.646 mm^{-1}	
F(000)	6592	

Table X3.2. Data collection and structure refinement for 3_Py4.

Theta range for data collection	1.52 to 20.82°	
Index ranges	-18<=h<=18, -19<=k<=22, -40<=l<=33	
Reflections collected	11276	
Independent reflections	3678 [R(int) = 0.0246]	
Max. and min. transmission	0.7446 and 0.6669	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3678 / 292 / 594	
Goodness-of-fit on F^2	1.052	
Final R indices	3182 data; I>2σ(I)	R1 = 0.0379, wR2 = 0.0990
	all data	R1 = 0.0450, wR2 = 0.1031
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0734P)^2+2.1930P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.030(14)	
Largest diff. peak and hole	0.210 and -0.154 $eÅ^{-3}$	

Table X3.3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for 3_Py4.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
N1	0.5111(3)	0.0309(2)	0.09333(17)	0.0628(15)
N3	0.5157(5)	0.1000(3)	0.17488(18)	0.094(2)
N6	0.3719(4)	0.0157(3)	0.14581(18)	0.0746(17)
C11	0.5726(4)	0.0427(3)	0.07479(19)	0.065(2)
C12	0.6024(5)	0.1006(3)	0.0759(2)	0.076(2)
C13	0.6668(6)	0.1140(4)	0.0595(3)	0.102(3)
C14	0.7035(6)	0.0730(5)	0.0406(3)	0.113(3)
C15	0.6733(6)	0.0170(4)	0.0380(2)	0.094(3)
C16	0.6111(5)	0.0025(3)	0.0544(2)	0.074(2)
N2	0.4141(7)	0.1555(5)	0.1078(4)	0.064(4)
C21	0.4315(7)	0.1656(5)	0.0756(3)	0.069(3)
C22	0.4118(7)	0.2169(5)	0.0601(4)	0.097(4)
C23	0.3720(8)	0.2595(7)	0.0787(5)	0.095(4)
C24	0.3528(10)	0.2489(10)	0.1094(6)	0.109(6)
C25	0.3745(7)	0.1949(6)	0.1246(4)	0.095(5)
Mn1	0.45956(6)	0.07410(4)	0.13104(10)	0.0662(4)
N2A	0.414(2)	0.1618(14)	0.1219(8)	0.107(18)
C21A	0.386(2)	0.1692(12)	0.0917(8)	0.091(15)
C22A	0.345(3)	0.2198(16)	0.0845(8)	0.117(17)
C23A	0.335(3)	0.2631(15)	0.1086(8)	0.15(2)
C24A	0.365(3)	0.2543(14)	0.1398(7)	0.156(18)
C25A	0.405(3)	0.2025(15)	0.1452(7)	0.167(19)
C41	0.4440(7)	0.0512(6)	0.2474(3)	0.086(3)
C42	0.4933(7)	0.0801(5)	0.2679(2)	0.085(3)
C43	0.4735(11)	0.1259(6)	0.2877(3)	0.116(5)
C44	0.4021(16)	0.1507(7)	0.2867(4)	0.161(8)
C45	0.3509(11)	0.1195(10)	0.2684(4)	0.175(9)
C46	0.3706(6)	0.0731(7)	0.2478(3)	0.105(4)
N4	0.4622(3)	0.0068(3)	0.22505(17)	0.0747(18)
C41A	0.434(4)	0.054(3)	0.2451(15)	0.080(18)
C42A	0.469(3)	0.103(3)	0.2587(15)	0.083(18)
C43A	0.435(3)	0.136(3)	0.2834(15)	0.080(18)
C44A	0.365(3)	0.119(3)	0.2943(15)	0.077(18)
C45A	0.330(3)	0.070(3)	0.2808(16)	0.076(18)
C46A	0.364(3)	0.037(3)	0.2562(15)	0.076(18)
N5	0.312(2)	0.911(2)	0.2003(12)	0.14(2)
C51	0.307(3)	0.895(2)	0.2319(11)	0.14(2)
C52	0.250(3)	0.858(3)	0.2422(10)	0.14(2)
C53	0.198(2)	0.840(2)	0.2193(12)	0.143(19)
C54	0.204(2)	0.857(2)	0.1865(12)	0.145(19)
C55	0.263(2)	0.894(2)	0.1778(11)	0.139(19)

	x/a	y/b	z/c	U(eq)
Mn2	0.40739(6)	0.96622(5)	0.18739(10)	0.0731(4)
N5A	0.3101(8)	0.9230(7)	0.2088(3)	0.102(4)
C51A	0.3187(10)	0.8737(7)	0.2273(3)	0.106(5)
C52A	0.2608(14)	0.8423(8)	0.2408(4)	0.116(6)
C53A	0.1926(12)	0.8666(11)	0.2383(4)	0.145(7)
C54A	0.1803(9)	0.9123(10)	0.2180(5)	0.179(9)
C55A	0.2402(9)	0.9417(7)	0.2046(4)	0.122(5)
C61	0.3035(5)	0.0427(3)	0.1461(2)	0.069(2)
C62	0.2890(6)	0.0860(5)	0.1698(3)	0.107(3)
C63	0.2203(8)	0.1125(5)	0.1720(4)	0.132(4)
C64	0.1640(10)	0.0977(7)	0.1501(4)	0.145(5)
C65	0.1796(7)	0.0586(9)	0.1262(4)	0.162(7)
C66	0.2487(6)	0.0287(5)	0.1238(2)	0.106(3)
C81	0.5090(8)	0.1657(8)	0.1782(5)	0.083(6)
C82	0.4687(10)	0.1970(7)	0.2015(4)	0.082(5)
C83	0.4718(11)	0.2565(10)	0.2047(5)	0.107(6)
C84	0.5217(13)	0.2869(10)	0.1860(6)	0.116(7)
C85	0.5653(14)	0.2562(10)	0.1623(7)	0.137(8)
C86	0.5571(10)	0.1944(10)	0.1596(5)	0.099(6)
C91	0.5635(18)	0.1546(9)	0.1752(5)	0.097(6)
C92	0.6257(15)	0.1626(9)	0.1525(4)	0.106(6)
C93	0.6667(15)	0.2126(9)	0.1535(5)	0.123(6)
C94	0.6540(17)	0.2569(10)	0.1743(6)	0.135(7)
C95	0.5942(18)	0.2509(10)	0.1965(6)	0.132(7)
C96	0.5533(16)	0.1994(8)	0.1970(5)	0.115(6)

Table X3.4. Bond lengths (Å) for 3_Py4.

N1-C11	1.375(9)	N1-N1	1.454(10)
N1-Mn1	2.040(6)	N3-C91	1.51(2)
N3-Mn2	2.111(7)	N3-Mn1	2.131(6)
N6-C61	1.386(10)	N6-Mn2	2.122(6)
N6-Mn1	2.156(6)	C11-C16	1.414(11)
C11-C12	1.417(10)	C12-C13	1.380(12)
C13-C14	1.375(14)	C14-C15	1.383(14)
C15-C16	1.352(12)	N2-C25	1.331(18)
N2-C21	1.362(19)	N2-Mn1	2.226(12)
C21-C22	1.367(15)	C22-C23	1.42(2)
C23-C24	1.31(3)	C24-C25	1.42(3)
Mn1-N2A	2.18(3)	N2A-C25A	1.327(14)
N2A-C21A	1.340(14)	C21A-C22A	1.390(13)

C22A-C23A	1.396(14)	C23A-C24A	1.395(14)
C24A-C25A	1.390(14)	C41-C42	1.387(15)
C41-N4	1.391(12)	C41-C46	1.426(15)
C42-C43	1.358(16)	C43-C44	1.41(2)
C44-C45	1.38(2)	C45-C46	1.387(19)
N4-N4	1.409(12)	N4-C41A	1.43(5)
N4-Mn2	2.040(6)	C41A-C42A	1.388(15)
C41A-C46A	1.41(4)	C42A-C43A	1.391(14)
C43A-C44A	1.390(14)	C44A-C45A	1.388(14)
C45A-C46A	1.392(14)	N5-C51	1.335(14)
N5-C55	1.336(14)	N5-Mn2	2.20(3)
C51-C52	1.392(14)	C52-C53	1.393(14)
C53-C54	1.389(14)	C54-C55	1.390(14)
Mn2-N3	2.111(7)	Mn2-N5A	2.199(12)
N5A-C51A	1.352(17)	N5A-C55A	1.352(19)
C51A-C52A	1.383(19)	C52A-C53A	1.36(3)
C53A-C54A	1.34(2)	C54A-C55A	1.386(18)
C61-C66	1.382(12)	C61-C62	1.396(13)
C62-C63	1.389(15)	C63-C64	1.395(19)
C64-C65	1.34(2)	C65-C66	1.431(18)
C81-C86	1.32(3)	C81-C82	1.39(2)
C82-C83	1.35(2)	C83-C84	1.37(3)
C84-C85	1.43(3)	C85-C86	1.41(3)
Table X3.4 (cont)			
C91-C96	1.35(3)	C91-C92	1.47(3)
C92-C93	1.36(2)	C93-C94	1.33(3)
C94-C95	1.42(4)	C95-C96	1.38(3)

Table X3.5. Bond angles (°) for 3_Py4.

C11-N1-N1	114.3(6)	C11-N1-Mn1	133.7(5)
N1-N1-Mn1	109.4(4)	C91-N3-Mn2	101.3(13)
C91-N3-Mn1	120.6(8)	Mn2-N3-Mn1	108.8(3)
C61-N6-Mn2	119.9(5)	C61-N6-Mn1	113.4(5)
Mn2-N6-Mn1	108.5(3)	N1-C11-C16	126.7(7)
N1-C11-C12	118.3(7)	C16-C11-C12	115.0(7)
C13-C12-C11	120.7(8)	C14-C13-C12	122.2(9)
C13-C14-C15	117.7(9)	C16-C15-C14	121.2(9)
C15-C16-C11	123.0(8)	C25-N2-C21	120.3(12)
C25-N2-Mn1	122.5(11)	C21-N2-Mn1	117.1(8)
N2-C21-C22	121.3(13)	C21-C22-C23	117.8(14)
C24-C23-C22	120.9(17)	C23-C24-C25	119.5(17)

N2-C25-C24	120.1(16)	N1-Mn1-N3	122.3(3)
N1-Mn1-N6	104.8(2)	N3-Mn1-N6	107.0(3)
N1-Mn1-N2A	118.9(10)	N3-Mn1-N2A	94.1(8)
N6-Mn1-N2A	108.9(12)	N1-Mn1-N2	104.5(4)
N3-Mn1-N2	107.6(4)	N6-Mn1-N2	110.4(4)
C25A-N2A-C21A	120.7(18)	C25A-N2A-Mn1	124.1(18)
C21A-N2A-Mn1	114.4(19)	N2A-C21A-C22A	120.0(16)
C21A-C22A-C23A	120.2(17)	C24A-C23A-C22A	118.6(17)
C25A-C24A-C23A	117.8(17)	N2A-C25A-C24A	122.7(18)
C42-C41-N4	125.2(11)	C42-C41-C46	115.8(10)
N4-C41-C46	118.8(10)	C43-C42-C41	122.8(13)
C42-C43-C44	121.9(13)	C45-C44-C43	115.5(13)
C44-C45-C46	122.3(16)	C45-C46-C41	120.8(13)
C41-N4-N4	112.9(7)	N4-N4-C41A	120.(3)
C41-N4-Mn2	133.9(6)	N4-N4-Mn2	112.3(4)
C41A-N4-Mn2	126.(3)	C42A-C41A-C46A	120.(2)
C42A-C41A-N4	131.(4)	C46A-C41A-N4	107.(4)
C41A-C42A-C43A	121.(2)	C44A-C43A-C42A	119.1(18)

Table X3.5 (cont)

C45A-C44A-C43A	120.8(19)	C44A-C45A-C46A	121.(2)
C45A-C46A-C41A	119.(2)	C51-N5-C55	122.2(19)
C51-N5-Mn2	115.(2)	C55-N5-Mn2	122.(2)
N5-C51-C52	119.8(18)	C51-C52-C53	119.1(18)
C54-C53-C52	119.7(18)	C53-C54-C55	118.4(17)
N5-C55-C54	120.8(18)	N4-Mn2-N3	100.0(3)
N4-Mn2-N6	120.4(2)	N3-Mn2-N6	112.7(3)
N4-Mn2-N5A	107.3(3)	N3-Mn2-N5A	108.3(5)
N6-Mn2-N5A	107.5(4)	N4-Mn2-N5	117.6(14)
N3-Mn2-N5	100.5(16)	N6-Mn2-N5	104.1(12)
C51A-N5A-C55A	115.8(12)	C51A-N5A-Mn2	119.4(12)
C55A-N5A-Mn2	124.7(10)	N5A-C51A-C52A	123.7(15)
C53A-C52A-C51A	117.3(16)	C54A-C53A-C52A	120.6(16)
C53A-C54A-C55A	118.6(17)	N5A-C55A-C54A	122.8(15)
C66-C61-N6	122.8(8)	C66-C61-C62	118.2(9)
N6-C61-C62	119.0(7)	C63-C62-C61	121.2(11)
C62-C63-C64	121.0(13)	C65-C64-C63	117.5(14)
C64-C65-C66	123.1(13)	C61-C66-C65	118.8(11)
C86-C81-C82	119.0(17)	C83-C82-C81	123.4(18)
C82-C83-C84	118.2(18)	C83-C84-C85	120.(2)
C86-C85-C84	118.(2)	C81-C86-C85	121.(2)
C96-C91-C92	114.9(19)	C96-C91-N3	123.(2)
C92-C91-N3	122.6(16)	C93-C92-C91	121.(2)

C94-C93-C92	123.(2)	C93-C94-C95	118.(2)
C96-C95-C94	120.(2)	C91-C96-C95	123.(2)

Table X3.6. Torsion angles (°) for 3_Py4.

N1-N1-C11-C16	5.4(10)	Mn1-N1-C11-C16	164.8(6)
N1-N1-C11-C12	-174.0(6)	Mn1-N1-C11-C12	-14.6(10)
N1-C11-C12-C13	175.8(8)	C16-C11-C12-C13	-3.6(11)
C11-C12-C13-C14	2.3(15)	C12-C13-C14-C15	0.6(16)
C13-C14-C15-C16	-1.9(16)	C14-C15-C16-C11	0.4(14)
N1-C11-C16-C15	-177.0(8)	C12-C11-C16-C15	2.4(11)
C25-N2-C21-C22	3.(2)	Mn1-N2-C21-C22	-173.9(9)
N2-C21-C22-C23	0.(2)	C21-C22-C23-C24	-2.(2)

Table X3.6 (cont)

C22-C23-C24-C25	2.(3)	C21-N2-C25-C24	-3.(2)
Mn1-N2-C25-C24	173.9(11)	C23-C24-C25-N2	0.(2)
C25A-N2A-C21A-C22A	0.0(5)	Mn1-N2A-C21A-C22A	170.(3)
N2A-C21A-C22A-C23A	0.0(4)	C21A-C22A-C23A-C24A	-0.1(10)
C22A-C23A-C24A-C25A	0.0(13)	C21A-N2A-C25A-C24A	0.0(10)
Mn1-N2A-C25A-C24A	-170.(3)	C23A-C24A-C25A-N2A	0.0(13)
N4-C41-C42-C43	175.5(10)	C46-C41-C42-C43	0.8(17)
C41-C42-C43-C44	-5.2(19)	C42-C43-C44-C45	10.(2)
C43-C44-C45-C46	-11.(3)	C44-C45-C46-C41	7.(3)
C42-C41-C46-C45	-1.5(19)	N4-C41-C46-C45	-176.6(12)
C42-C41-N4-N4	-0.3(14)	C46-C41-N4-N4	174.3(11)
C42-C41-N4-C41A	-160.(20)	C46-C41-N4-C41A	20.(20)
C42-C41-N4-Mn2	-168.5(8)	C46-C41-N4-Mn2	6.1(17)
C41-N4-C41A-C42A	45.(17)	N4-N4-C41A-C42A	22.(6)
Mn2-N4-C41A-C42A	-144.(4)	C41-N4-C41A-C46A	-120.(20)
N4-N4-C41A-C46A	-145.(3)	Mn2-N4-C41A-C46A	49.(4)
C46A-C41A-C42A-C43A	0.0(4)	N4-C41A-C42A-C43A	-166.(7)
C41A-C42A-C43A-C44A	0.1(4)	C42A-C43A-C44A-C45A	-0.2(10)
C43A-C44A-C45A-C46A	0.3(13)	C44A-C45A-C46A-C41A	-0.2(13)
C42A-C41A-C46A-C45A	0.0(9)	N4-C41A-C46A-C45A	169.(6)
C55-N5-C51-C52	0.0(5)	Mn2-N5-C51-C52	-178.(4)
N5-C51-C52-C53	0.0(4)	C51-C52-C53-C54	-0.1(10)
C52-C53-C54-C55	0.2(13)	C51-N5-C55-C54	0.1(10)
Mn2-N5-C55-C54	178.(4)	C53-C54-C55-N5	-0.2(13)
C55A-N5A-C51A-C52A	1.(2)	Mn2-N5A-C51A-C52A	-177.8(10)
N5A-C51A-C52A-C53A	-7.(2)	C51A-C52A-C53A-C54A	13.(3)
C52A-C53A-C54A-C55A	-12.(3)	C51A-N5A-C55A-C54A	-1.(2)
Mn2-N5A-C55A-C54A	178.5(14)	C53A-C54A-C55A-N5A	6.(3)

Mn2-N6-C61-C66	-118.5(7)	Mn1-N6-C61-C66	111.1(7)
Mn2-N6-C61-C62	61.7(9)	Mn1-N6-C61-C62	-68.6(8)
C66-C61-C62-C63	3.1(14)	N6-C61-C62-C63	-177.2(9)
C61-C62-C63-C64	-1.5(17)	C62-C63-C64-C65	-2.(2)
C63-C64-C65-C66	5.(2)	N6-C61-C66-C65	179.5(8)
C62-C61-C66-C65	-0.8(12)	C64-C65-C66-C61	-3.3(18)
C86-C81-C82-C83	5.(3)	C81-C82-C83-C84	-6.(3)
C82-C83-C84-C85	4.(3)	C83-C84-C85-C86	-2.(4)
C82-C81-C86-C85	-3.(3)	C84-C85-C86-C81	1.(3)

Table X3.6 (cont)

Mn2-N3-C91-C96	-116.(2)	Mn1-N3-C91-C96	124.(2)
Mn2-N3-C91-C92	63.(2)	Mn1-N3-C91-C92	-57.(3)
C96-C91-C92-C93	-2.(4)	N3-C91-C92-C93	179.(2)
C91-C92-C93-C94	0.(4)	C92-C93-C94-C95	0.(4)
C93-C94-C95-C96	3.(4)	C92-C91-C96-C95	5.(4)
N3-C91-C96-C95	-177.(2)	C94-C95-C96-C91	-5.(4)