Electronic Supplementary Material (ESI) for Dalton Transactions.

Stepwise Spin-State Switching in a Manganese(III) Complex

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Experimental Section

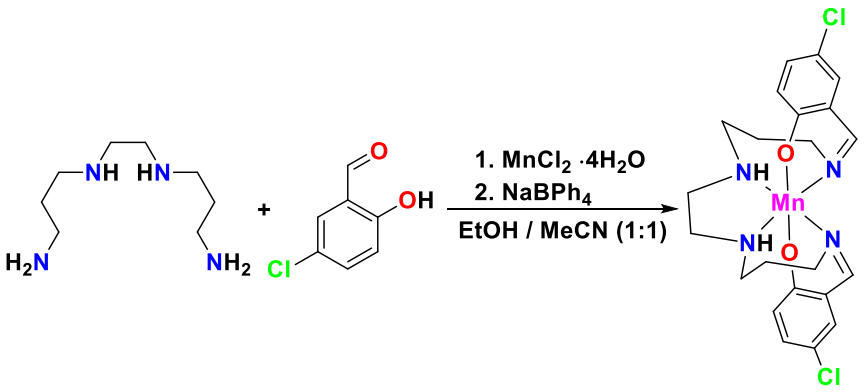
Materials and physical measurements

All manipulations were carried out in air unless otherwise stated. Solvents were dried by standard methods and freshly distilled before to use. All chemicals were used as purchased from various chemical sources without further purification. The crystals of the complex were removed from the mother liquor and dried on filter paper to remove any adhering solvent molecules, before to measurement. The elemental analysis of C, H, and N were performed with Thermo Scientific Flash 2000 Organic Elemental Analyzer. Infrared (IR) spectra were recorded in the range of 4000 – 400 cm^{-1} on Bruker Tensor 27 spectrometer. UV-vis-NIR spectra were carried out in the region of 250 – 2000 nm on a Lambda 750 UV-vis-NIR spectrometer. The UV-vis spectroscopic measurements in solution were done in quartz cuvettes with a path length of 1 cm. Solid-state measurement was carried out by taking 5% sample by weight in KBr. Thermogravimetric analysis (TGA) was done on a Mettler Toledo TGA/SDTA851 analyzer with a heating rate of 10 K min^{-1} under a nitrogen atmosphere ranging from 303 to 573 K. Differential scanning calorimetry (DSC) measurements were performed using Mettler Toledo DSC 823^e differential scanning calorimeter with a scan rate of 5 K min^{-1} in a nitrogen atmosphere in the temperature range of 300 K to 140 K (lowest measurable temperature). Powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical Empyrean diffractometer at 45 kV and 30 mA, under Cu-Kα radiation (λ = 1.54059 Å). PXRD data analyses were done using PANalytical X'Pert HighScore Plus software.[1] Electrochemistry experiments (cyclic voltammetry (CV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) measurements were performed with a Metrohm Autolab PGSTAT101 using platinum as working electrode with the sample (~1 mM) in acetonitrile with 0.2 M (^{n}Bu$_4$N)PF$_6$ as supporting electrolyte. Ferrocene was used as an internal reference.

Synthesis of complex

[Mn(5Cl-sal$_2$-323)](BPh$_4$) (1). Under an aerobic environment, a solution of 5-chloro-2-hydroxybenzaldehyde (31.2 mg, 0.2 mmol) in a mixture of ethanol and acetonitrile (1:1, 5 mL) was added to a stirred solution of N,N′- bis(3-aminopropyl)ethylenediamine (17.4 mg, 0.1 mmol)

in same solvents mixture (5 mL). The reaction mixture was stirred for 10 min to obtain a bright yellow solution. Then, a solution of manganese(II) chloride tetrahydrate (19.8 mg, 0.1 mmol) in ethanol/MeCN (1:1, 5 mL) was added; the solution color changed from yellow to deep brown indicating the aerobic oxidation of Mn(II) to Mn(III), and the reaction mixture was stirred for another 10 min. A solution of sodium tetraphenylborate (34.5 mg, 0.1 mmol) in ethanol/MeCN (1:1, 5 mL) was added and the reaction mixture was stirred for 2 h. After filtration, the brown filtrate was kept for slow evaporation to obtain analytically pure block shape crystals of **1** in 75% yield. Formula for **1**: $C_{46}H_{46}BCl_2MnN_4O_2$ (MW. 823.52 $gmol^{-1}$): Anal. Calcd. C 67.09, H 5.63, N 6.80; found C 67.23, H 5.89, N 6.48; ATR-IR (only intensive bands): ν (cm^{-1}) = 3243, 3051, 1618, 1536, 1465, 1423, 1369, 1282, 1190, 1073, 1048, 979, 889, 861, 828, 803, 751, 733, 703, 666, 611, 583, 557, 488, 457, 447.



Scheme 1. Synthetic scheme for **1**.

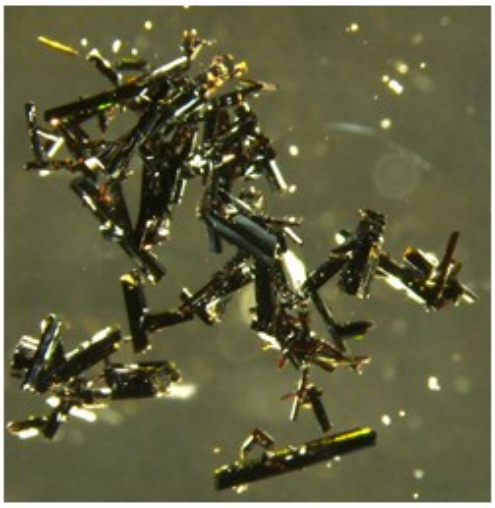


Fig. S1. Picture of crystals for complex **1**.

Magnetic Measurements

The magnetic susceptibility measurements were carried out with Quantum Design MPMS-XL EverCool SQUID magnetometer, between 2 and 300 K for dc applied fields ranging from -5 T to 5 T for **1**. Polycrystalline sample of **1** (25.67 mg) introduced in a polyethylene bag (2.8 × 0.75 × 0.02 cm) were subjected to measurements. The temperature dependent data were measured using 10000 Oe dc field. The isothermal magnetization data were acquired at 4 and 6 K. *M vs H* measurements were performed at 100 K to check for the presence of ferromagnetic impurities which were found to be absent. The magnetic data were corrected for the sample holder and the diamagnetic contribution.

X-ray crystallography

Single crystal X-ray structure analyses data of the complex **1** were collected with a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). The single crystal was mounted on crystal mounting loop with the help of Paratone oil at 240 K followed by data collection. The same crystal was slowly cooled down to 120 K and 100 K with 2 K / min ramping rate, followed by data collection. Data integration and reduction were performed with the help of SAINT software and empirical absorption corrections were applied with SADABS programme.[2] The structures at 120 K and 240 K were solved using intrinsic phasing methods with *Shel*XT[3] and refined with a full-matrix least-squares method on F^2 using *Shel*XL-2018[4] in *OLEX*[2] *GUI*.[5] The 100 K data was solved using charge flipping method and refined with L-M method using *OLEX*[2]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were labeled to ideal positions and refined isotropically. Hydrogen atoms were constrained by geometry. To handle the atomic position disorder of C atoms in the phenyl ring of BPh_4^- counter anion, C atoms of phenyl rings were refined with a free variable associated with the occupancy. The total sum occupancy for the different parts of the same C atoms was constrained to be 1. The PART instruction has been used to constrain the equivalent atomic displacement parameter. Additionally, RIGU, SIMU and ISOR restraints have also been used for appropriate carbon atoms with anisotropic refinement in *Shel*XL.

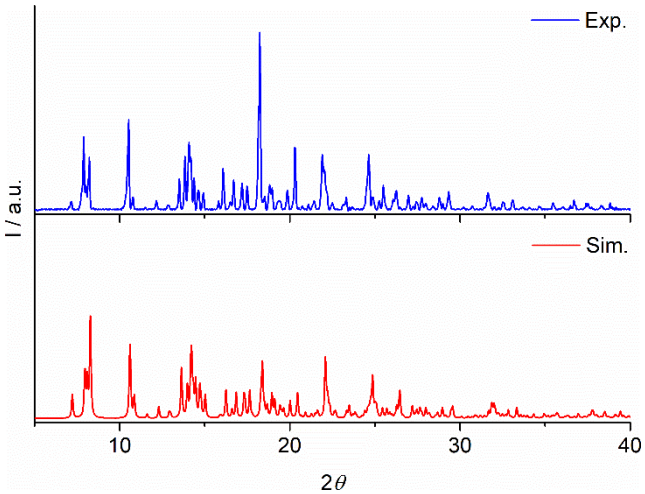


Fig. S2. Comparison of the room temperature experimental PXRD pattern and the 240 K simulated one for **1**.

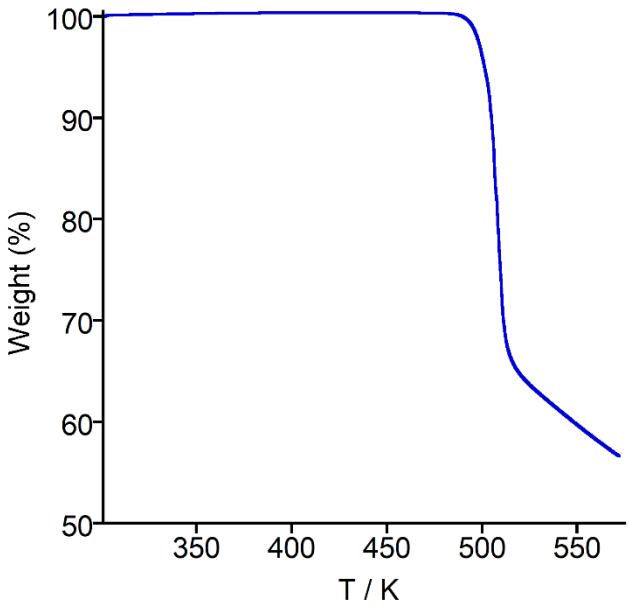


Fig. S3. TGA curve for **1** from 303 K to 573 K at a 10 K min^{-1} temperature rate under N_2 atmosphere.

Spectroscopic studies

Complex **1** was characterized by solid state IR spectroscopy at room temperature (Fig. S4). The IR spectrum shows characteristic C=N and N–H stretching vibrations of coordinated Schiff-base ligand at around 1618 cm^{-1} and 3243 cm^{-1} respectively, while the peak at around 730 and 705 cm^{-1} suggested the presence of BPh_4^- anion in **1**. In addition, IR spectrum displays typical absorption of coordinated Schiff-base ligand at around 1595, 1540, 1460, 1423, 1370, 1280, 1072, 1048, 860, 705 and 560 cm^{-1}.

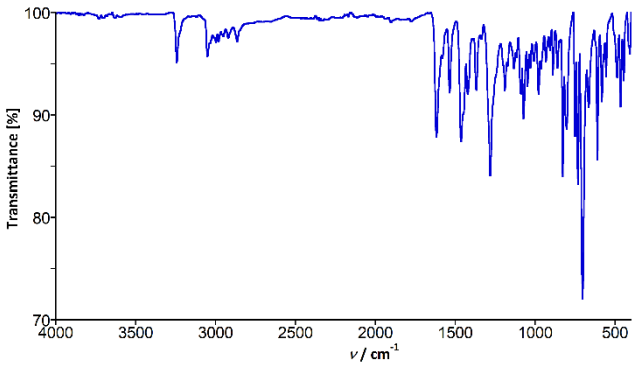


Fig. S4. ATR spectrum of **1** at RT.

Electronic absorption spectroscopic studies were carried out on **1** in solid-state as well as in solution at room temperature (Fig. S5 and S6). UV-vis-NIR spectra in acetonitrile exhibit one broad band along with two shoulders at around 1100 nm, 650 nm and 580 nm respectively which are attributed to *d-d* transitions ($^5A_{1g} \rightarrow {}^5B_{1g}$, $^5A_{1g} \rightarrow {}^5E_g$ and $^5A_{1g} \rightarrow {}^5B_{2g}$) from HS Mn(III) ion in a tetragonally compress octahedral system. The higher molar coefficient of the later band could be explained by the tailing effect from nearby ligand-to-metal charge transfer (LMCT) transition. Apart from *d-d* transitions, UV-vis-NIR spectrum reveals phenolate ligand-based LMCT transition at around 520 nm, nitrogen donor ligand-based LMCT transition near 340 nm and intra-ligand charge transfer (ILCT) transition nearly at around 270 nm. The solid-state spectrum (Fig. S6) of **1** also exhibits very similar absorption bands with the solution spectrum, suggested that the complex well-preserved its identity upon dissolution.

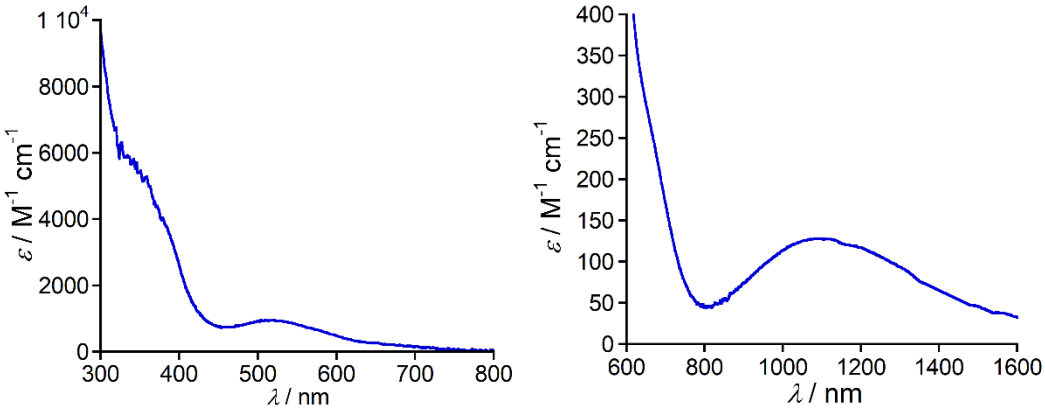


Fig. S5. UV-vis-NIR spectra of **1** in MeCN with dilute (left) and concentrated (right) solution at room temperature.

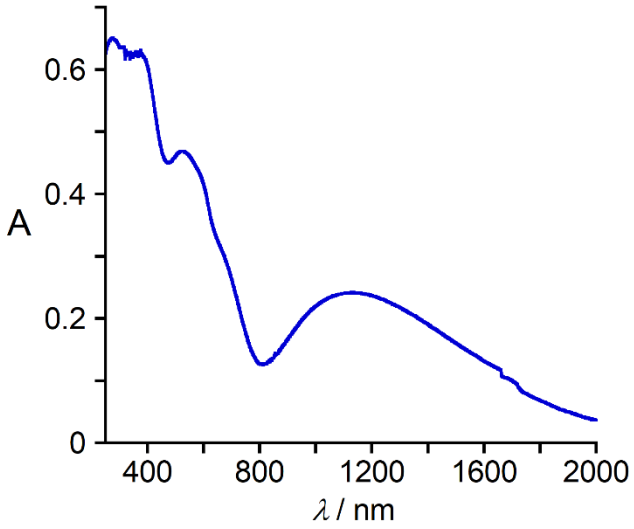


Fig. S6. Solid state UV-vis-NIR spectrum of **1** in KBr at room temperature.

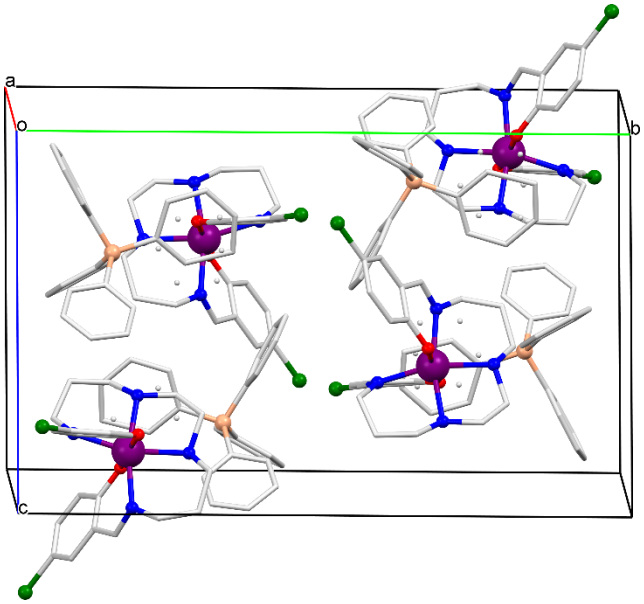


Fig. S7. Perspective view of unit cell in **1** at 240 K. Hydrogen atoms are omitted for clarity (Mn: Purple, C: grey, N: blue, O: red, Cl: green).

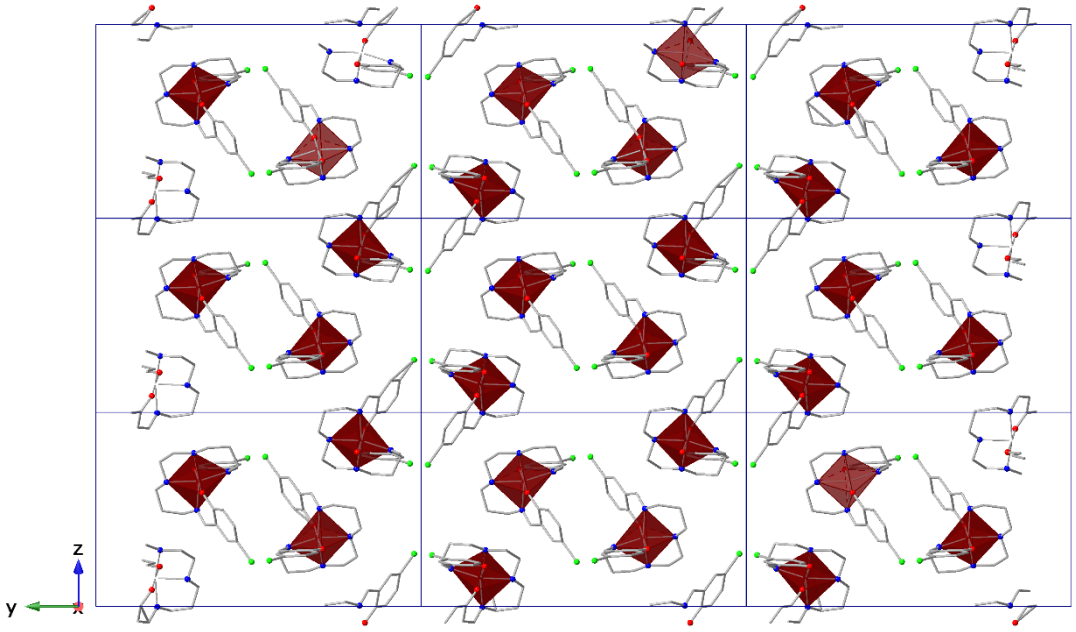


Fig. S8. Perspective view of unit cell packing along the *a*-axis in **1** at 240 K. Counter-anions and hydrogen atoms are omitted for clarity (Mn(HS), maroon, polyhedral environment).

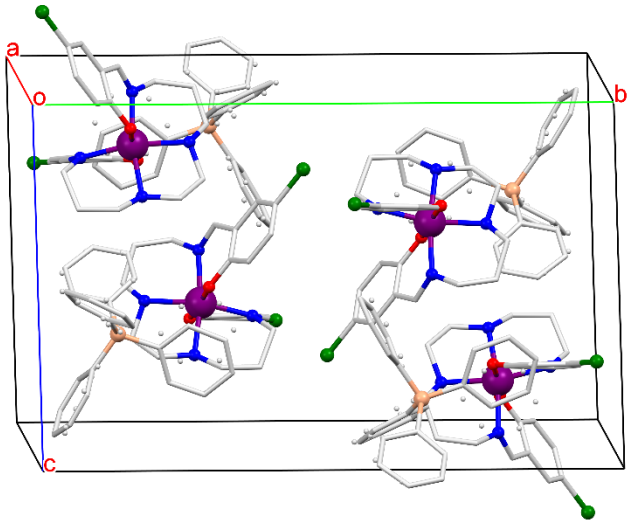


Fig. S9. Perspective view of unit cell in **1** at 120 K. Hydrogen atoms are omitted for clarity (Mn: Purple, C: grey, N: blue, O: red, Cl: green).

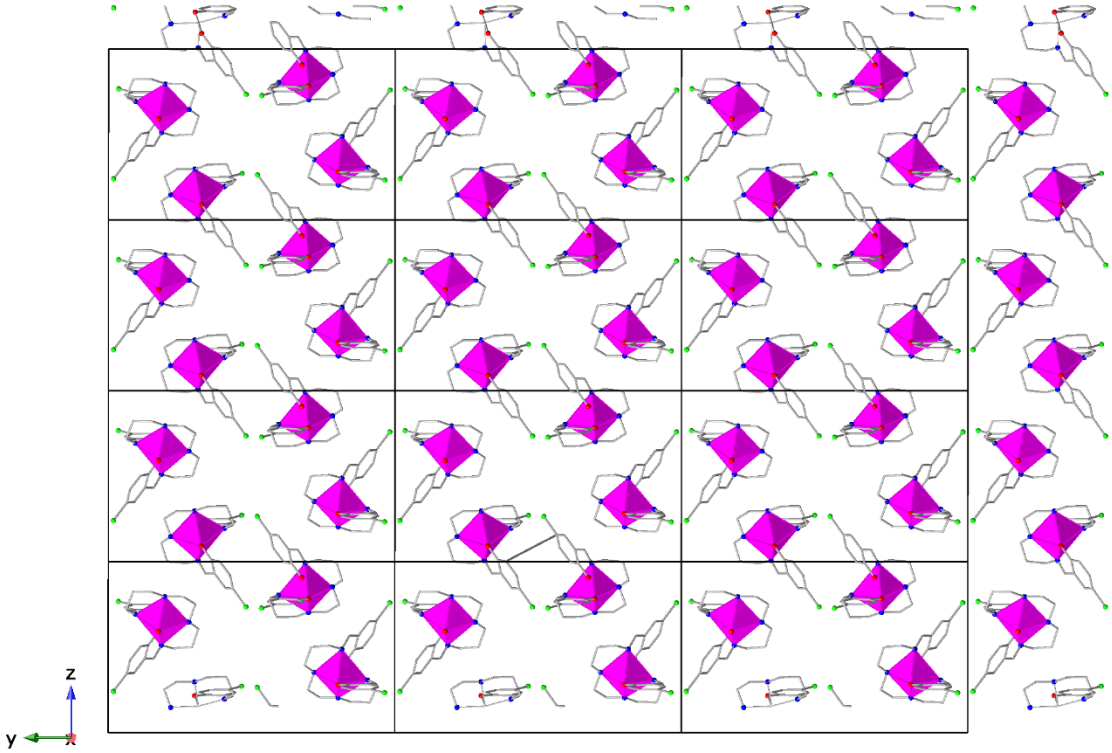


Fig. S10. Perspective view of unit cell packing along the *a*-axis in **1** at 120 K. Counter-anions and hydrogen atoms are omitted for clarity (Mn(intermediate), violet, polyhedral environment).

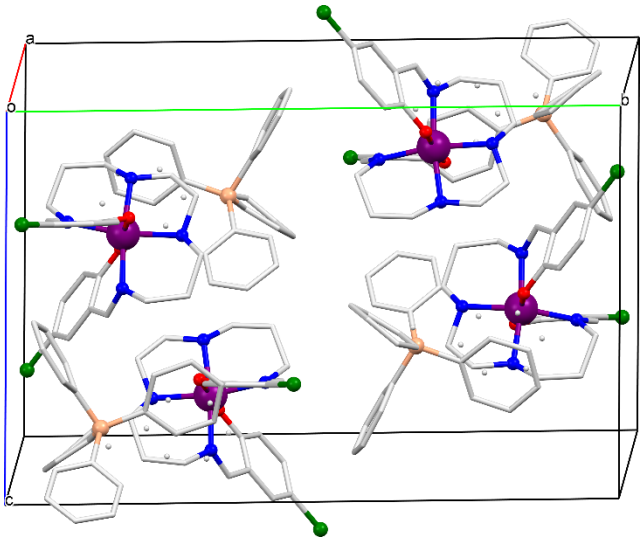


Fig. S11. Perspective view of unit cell in **1** at 100 K. Hydrogen atoms are omitted for clarity (Mn: Purple, C: grey, N: blue, O: red, Cl: green).

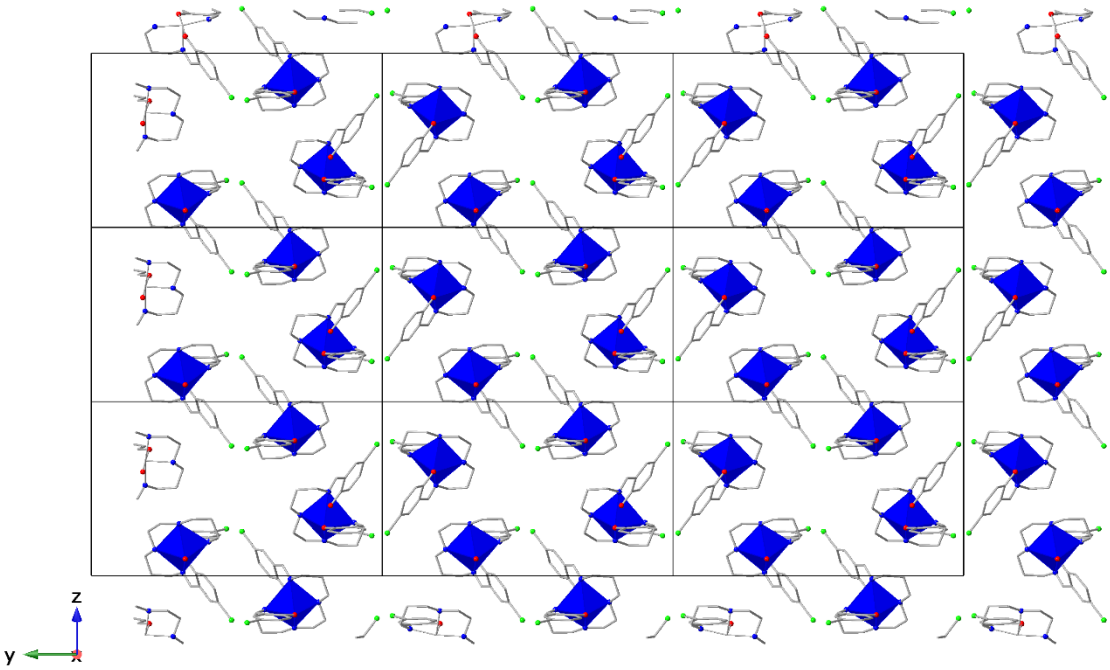


Fig. S12. Perspective view of unit cell packing along the *a*-axis in **1** at 100 K. Counter-anions and hydrogen atoms are omitted for clarity (Mn(LS), blue, polyhedral environment).

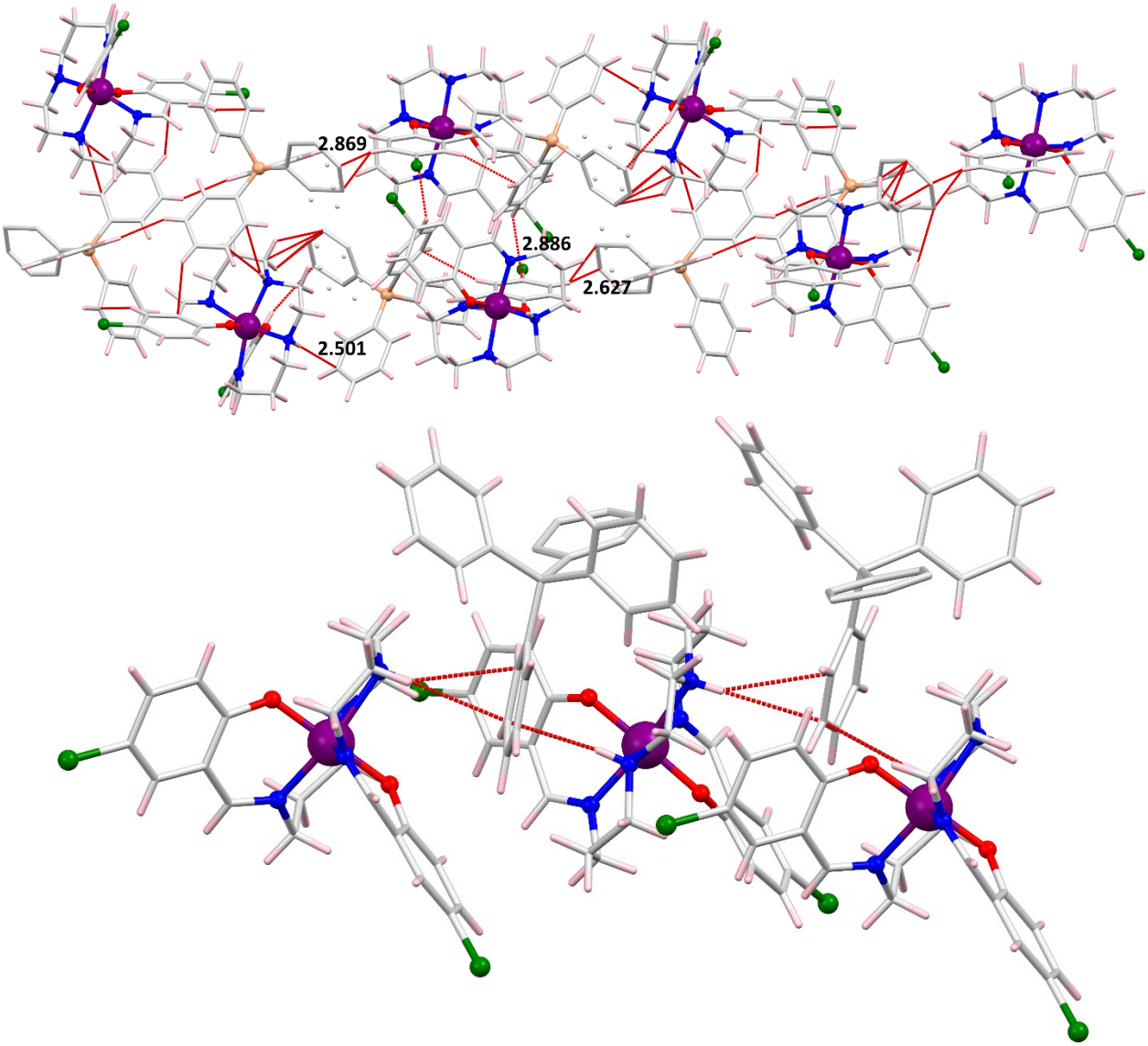


Fig. S13. Top: Perspective view of a fragment of the supramolecular structure displaying several weak interactions (red lines) in **1** at 240 K. Bottom: View of N–H···C interactions forming 1D chain in **1** at 240 K.

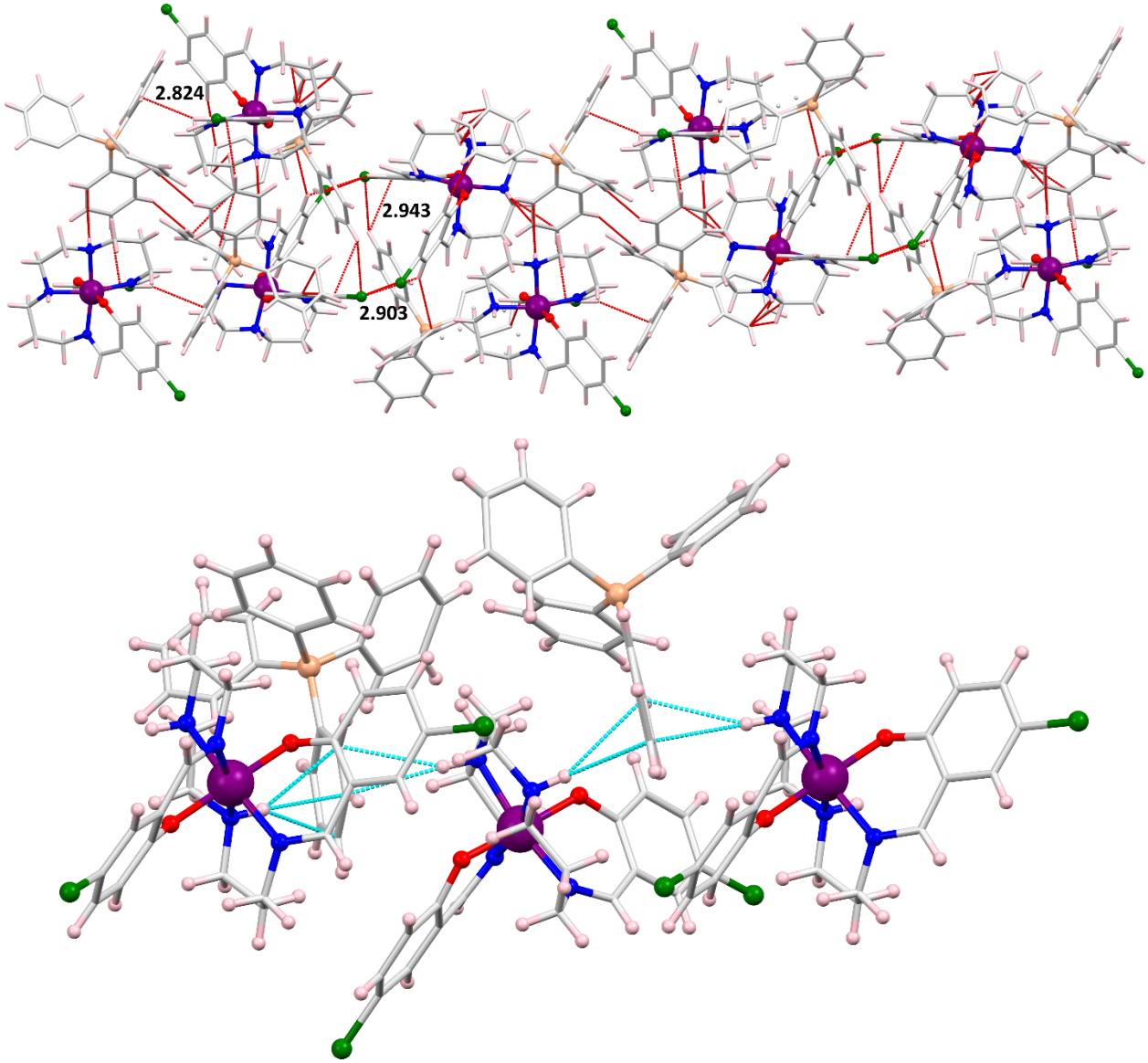


Fig. S14. Perspective view of a fragment of the supramolecular structure displaying several weak interactions (red lines) in **1** at 120 K. Bottom: View of N–H···C interactions forming 1D chain in **1** at 120 K.

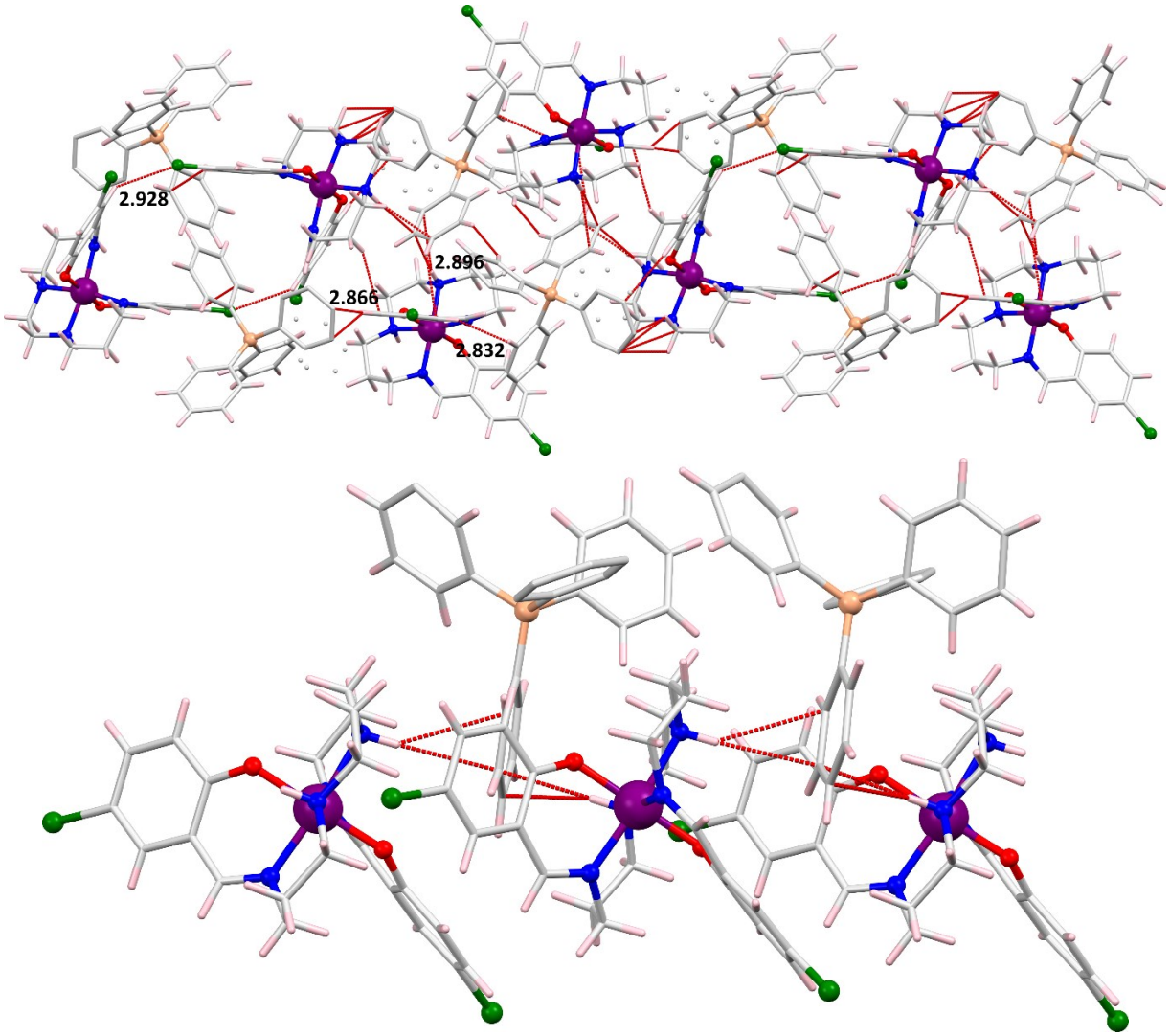


Fig. S15. Top: Perspective view of a fragment of the supramolecular structure displaying several weak interactions (red lines) in **1** at 100 K. Bottom: View of N–H···C interactions forming 1D chain in **1** at 100 K.

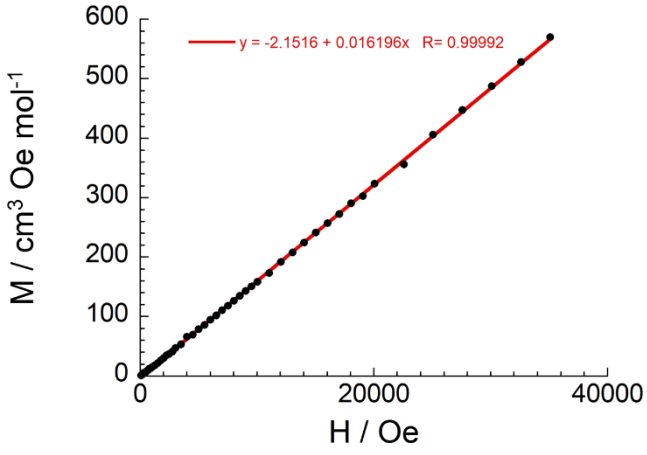


Fig. S16. Field dependence of the magnetization as *M vs H* plots for **1** at 100 K. The solid line is best fit.

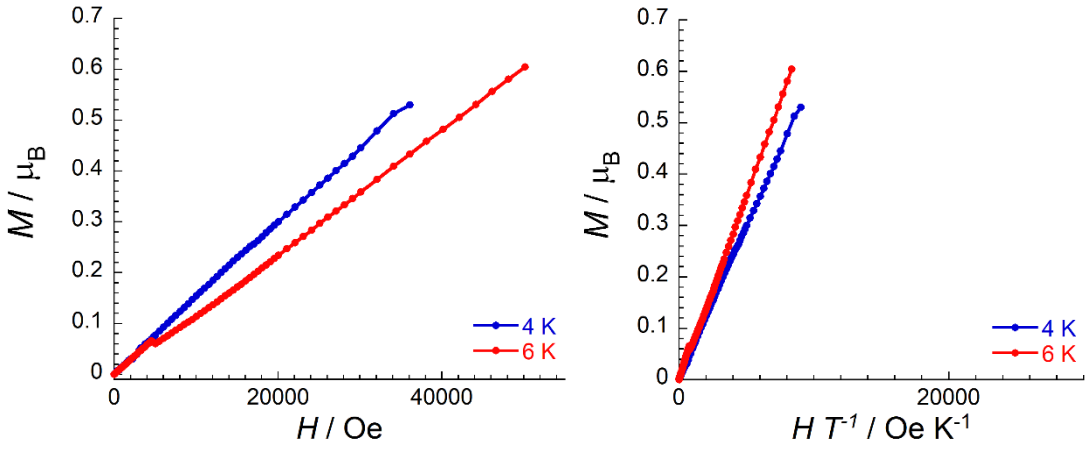


Fig. S17. Field dependence of the magnetization as *M* vs *H* (left) and *M* vs *H/T* (right) plots for **1** at 4 and 6 K. The solid lines are guide for the eyes.

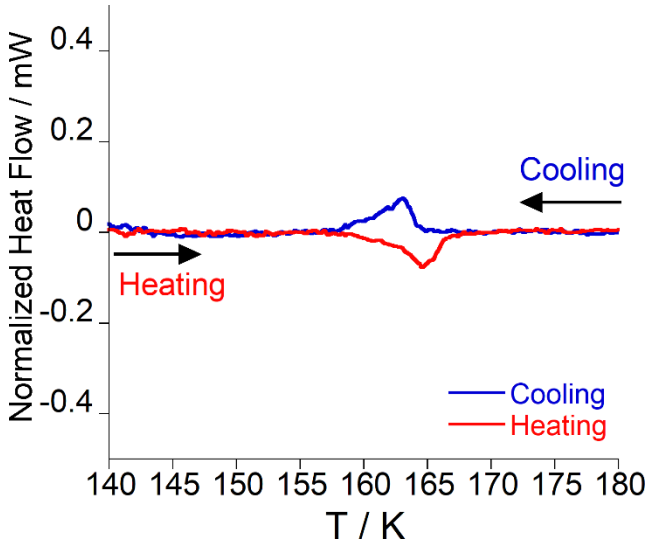


Fig. S18. DSC plot of **1** shown between 180 and 140 K at a sweep rate of 5 K min^{-1}.

Note: DSC data in the low-temperature region up to 100 K are not available due to the temperature limitation of our instrument.

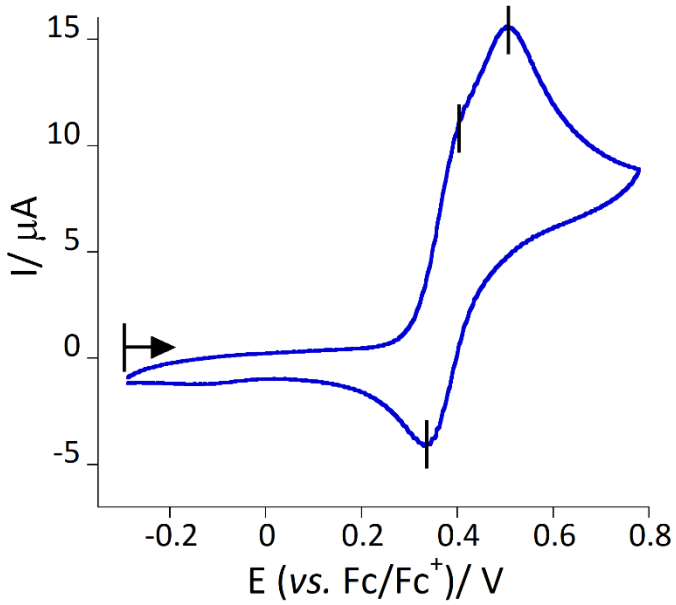


Fig. S19. Cyclic voltammogram for oxidation of **1** in 0.2 M (^{n}Bu$_4$N)PF$_6$/MeCN with a scan rate of 100 mV s^{-1}. Arrow indicates the open circuit potential with the direction of the potential sweep.

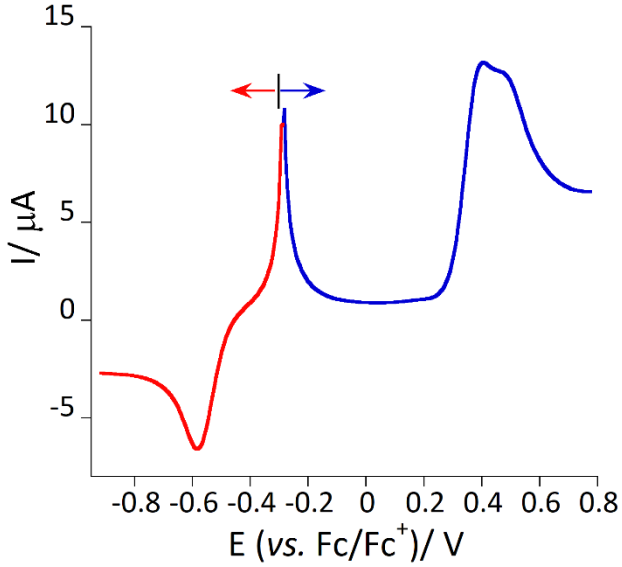


Fig. S20. Square wave voltammograms for **1** in 0.2 M (^{n}Bu$_4$N)PF$_6$/MeCN. Arrows indicate the open circuit potential with the direction of the potential sweep.

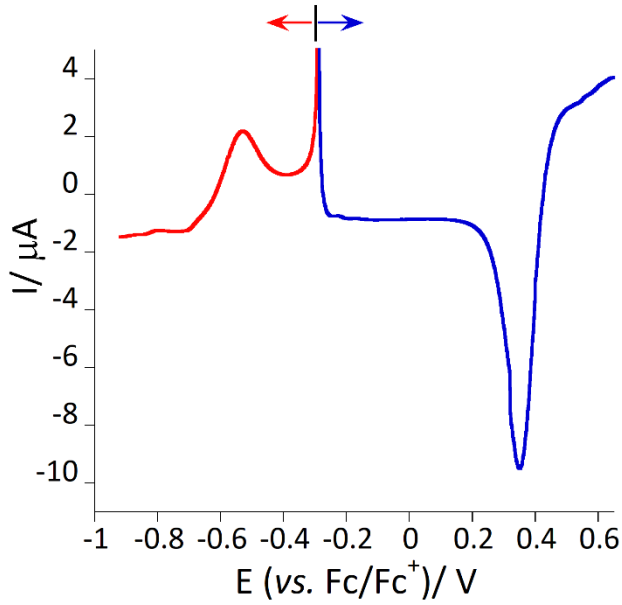


Fig. S21. Differential pulse voltammograms for **1** in 0.2 M (^{n}Bu$_4$N)PF$_6$/MeCN. Arrows indicate the open circuit potential with the direction of the potential sweep.

Cyclic voltammograms and square wave voltammogram of $NaBPh_4$ show an irreversible at around E_{pc}= 0.51 V *vs* Fc/Fc^+ (Fig. S22 and S23).

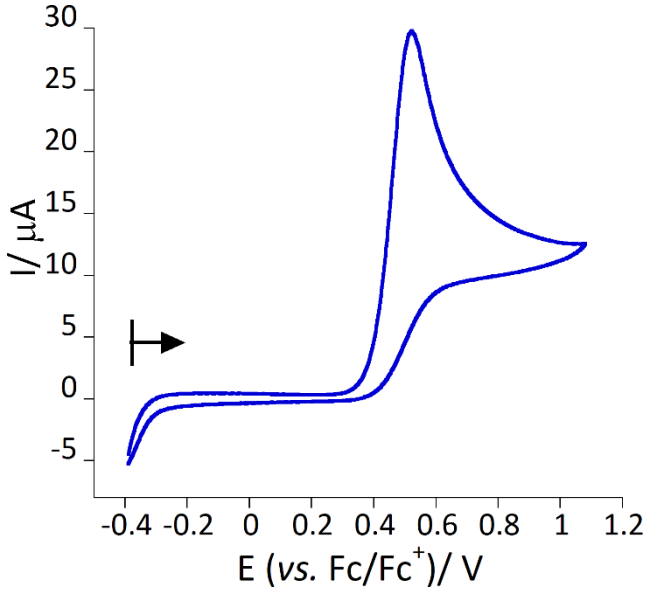


Fig. S22. Cyclic voltammogram for oxidation of $NaBPh_4$ in 0.2 M (^{n}Bu$_4$N)PF_6/MeCN with a scan rate of 100 mV s^{-1}. Arrow indicates the open circuit potential with the direction of the potential sweep.

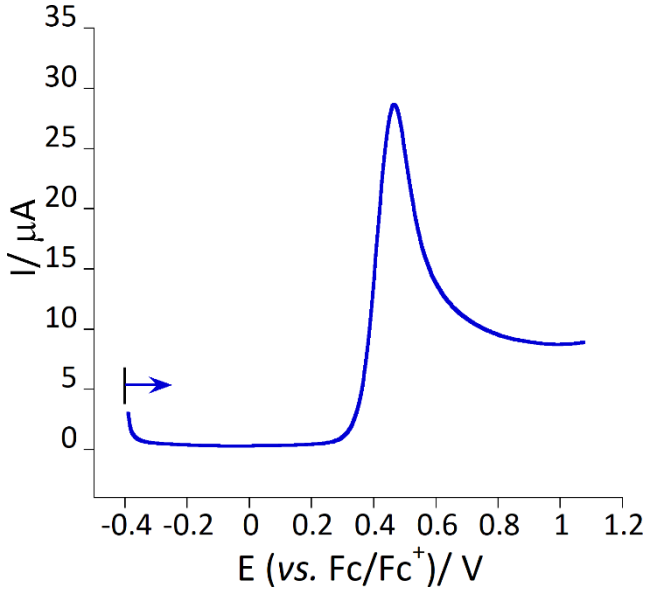


Fig. S23. Square wave voltammogram for oxidation of $NaBPh_4$ in 0.2 M (^{n}Bu$_4$N)PF_6/MeCN. Arrow indicates the open circuit potential with the direction of the potential sweep.

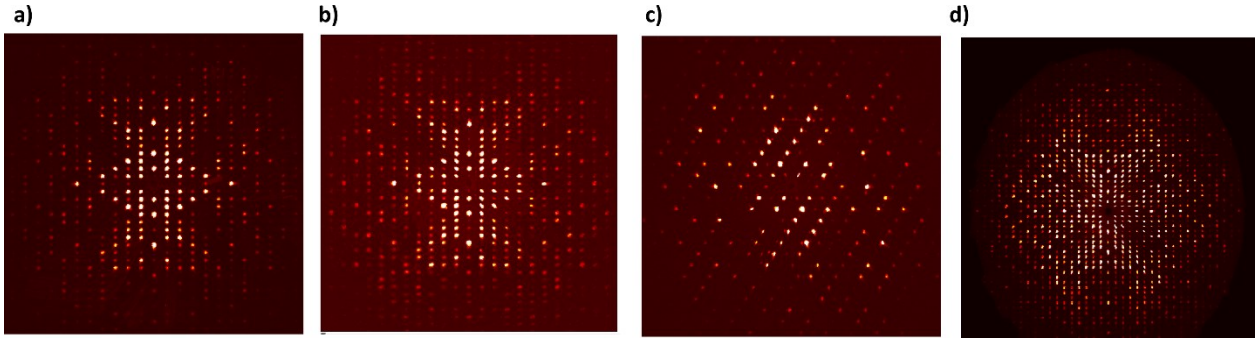


Fig. S24. Precession images from **1** in the *hk0* at 240 K (monoclinic, a), 120 K (monoclinic, b), 120 K (triclinic, c) and 100 K (monoclinic, d)

Table

Table S1. X-ray crystallography data for complex **1**.

Complex	**1**		
CCDC no	**2015524**	**2015521**	**2015472**
temp (K)	240	120	100
empirical formula	$C_{46}H_{46}BCl_2MnN_4O_2$	$C_{46}H_{46}BCl_2MnN_4O_2$	$C_{46}H_{46}BCl_2MnN_4O_2$
formula wt	823.52	823.52	823.52
cryst syst	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	14.3566(10)	14.2615(10)	14.2627(5)
b (Å)	21.8039(15)	21.6350(14)	21.6172(8)
c (Å)	14.4656(11)	14.4098(10)	14.4837(5)
α (deg)	90	90	90
β (deg)	116.203(3)	116.523(2)	116.711(2)
γ (deg)	90	90	90
V, Å^3	4062.8(5)	3978.2(5)	3989.1(3)
Z	4	4	4
d_{calcd} (g cm^{-3})	1.346	1.375	1.365
μ (mm^{-1})	0.501	0.511	0.510
F(000)	1720	1720	1723
θ_{max} (deg)	25	26.50	30.74
completeness (%)	100	100	99.6
no. of. rflns collected	7143	8238	12377
no. of. Indep rflns	4763	5405	10956
goodness of fit on F^2	1.014	1.128	1.054
final R indices (I>2σ(I))	R1 = 0.0456 wR2 = 0.0940	R1 = 0.0768 wR2 = 0.1560	R1 = 0.0438 wR2 = 0.0937
final R indices (all data)	R1 = 0.0840 wR2 = 0.1148	R1 = 0.1117 wR2 = 0.1648	R1 = 0.0505 wR2 = 0.0976

Table S2. Selected bond distances (Å) and bond angles (°) in **1**.

	1		
	240 K	**120 K**	**100 K**
Mn(1)-N(1)	2.168(3)	2.111(4)	2.0752(14)
Mn(1)-N(2)	2.179(3)	2.112(4)	2.0809(13)
Mn(1)-N(3)	2.060(3)	2.013(4)	2.0010(14)
Mn(1)-N(4)	2.095(3)	2.034(5)	2.0085(14)
Mn(1)-O(1)	1.853(2)	1.858(3)	1.8750(11)
Mn(1)-O(2)	1.864(2)	1.864(3)	1.8667(11)
N(1)-Mn(1)-N(2)	81.05(11)	82.73(17)	83.91(5)
N(1)-Mn(1)-N(3)	164.19(11)	167.96(17)	169.98(5)
N(1)-Mn(1)-N(4)	85.90(11)	87.91(18)	88.96(6)
N(1)-Mn(1)-O(1)	84.79(10)	84.92(16)	84.92(5)
N(1)-Mn(1)-O(2)	93.01(10)	91.93(16)	91.79(5)
N(2)-Mn(1)-N(3)	85.06(11)	86.89(17)	87.80(6)
N(2)-Mn(1)-N(4)	165.13(11)	169.12(18)	171.39(6)
N(2)-Mn(1)-O(1)	93.21(10)	91.98(16)	91.62(5)
N(2)-Mn(1)-O(2)	86.85(10)	87.10(15)	91.65(5)
N(3)-Mn(1)-N(4)	108.74(10)	102.98(18)	87.10(5)
N(3)-Mn(1)-O(1)	88.49(9)	89.39(16)	89.70(5)
N(3)-Mn(1)-O(2)	93.74(10)	93.61(16)	93.42(5)
N(4)-Mn(1)-O(1)	92.67(10)	92.70(16)	92.53(5)
N(4)-Mn(1)-O(2)	86.74(10)	87.69(16)	88.31(5)
O(1)-Mn(1)-O(2)	177.76(10)	176.81(16)	176.59(5)

Continuous Shape Measures (CShM) Analysis:

Continuous Shape Measures (CShM) analysis was carried out to determine the geometry around Mn(III) ion. Based on the values obtained, the idealized polyhedron was matched with the actual coordination spheres. The smallest value is symbolic of proximity of actual coordination sphere and idealized polyhedron.

Table S3: CShM analysis data for complex **1**.

Complex	Temp.	Structure				
		HP - 6	PPY - 6	**OC - 6**	TPR - 6	JPPY - 6
2	240 K	32.110	24.624	**1.281**	11.344	27.401
	120 K	32.463	26.495	**0.691**	12.864	29.427
	100 K	32.699	27.525	**0.464**	13.643	30.577

HP – 6: Hexagon (D6h), PPY – 6 = Pentagonal pyramid, OC – 6: Octahedron (Oh), TPR – 6: Trigonal prism (D3h), JPPY – 6 = Johnson pentagonal pyramid J2 (C5v);

Octahedral Distortion Parameters

$\sum$ is the sum of the deviation from 90° of the 12 *cis*-angles of the MnN_4O_2 octahedron; Θ is the sum of the deviation from 60° of the 24 trigonal angles of the projection of the MnN_4O_2 octahedron onto the trigonal faces; ζ is the distance distortion parameter, which is the sum of deviation from individual M-N/O bond distances with respect to the mean metal-ligand bond distance.

Table S4. Spin crossover behaviors of [Mn(X-sal$_2$-323)](BPh$_4$) (X = ligand substituent) complexes with associated Mn–N/O bond distances

Complex **X**	$T_{1/2}$ (K)[a]	T (K)[b]	Mn–O (Å)	Mn–N (Å)	Spin State	Ref.
[Mn(5Cl-sal$_2$-323)](BPh$_4$) **X = 5-Cl**	$T_{1/2}$ (1) = 168 K $T_{1/2}$ (2) = 103 K Two-step and complete	100 120 240	1.8753(13)-1.8661(13) 1.856(4)-1.864(4) 1.865(4)-1.861(4) 1.8650(19)-1.8540(19)	2.0742(18)-2.0808(16) 2.0005(17)-2.0085(17) 2.139(5)-2.121(5) 2.047(5)2.022(5) 2.098(5)-2.101(5) 2.005(5)-2.018(5) 2.167(3)-2.179(3) 2.060(2)-2.095(3)	LS HS]:[LS] (1:1) HS	This work
[Mn(3,5-diBr-sal$_2$(323))](BPh$_4$) **X = 3,5-diBr**	$T_{1/2}\downarrow$ = 82 $T_{1/2}\uparrow$ = 90 ΔT=8 K hysteretic and abrupt [HS][HS] to [HS][LS] (1:1)	25 83 110 150 250 293	1.868(14)-1.908(15) 1.875(7)-1.892(7) 1.868(2)-1.879(2) 1.866(3)-1.879(3) 1.864(3)-1.879(3) 1.866(3)-1.876(4)	2.008(18)-2.08(2), 2.058(16)-1.99(2) 2.002(8)-2.082(9) 2.059(8)-2.002(10) 2.101(3)-2.262(3) 2.209(3)-2.094(3) 2.098(3)-2.259(4) 2.206(4)-2.090(4) 2.102(4)-2.232(5) 2.218(5)-2.075(5) 2.104(4)-2.230(5) 2.221(5)-2.079(5)	HS:LS (1:1) HS:LS (1:1) HS HS HS HS	[6]
[Mn(3-OEt-Sal-323)](BPh$_4$) **X = 3-OEt**	HS	100	1.8687(10)-1.8586(10)	2.0950(11)-2.2479(12)	HS	[7]
[Mn(3-OMe-sal$_2$-323)](BPh$_4$) **X = 3-OMe**	HS	100	1.8516(18)-1.8829(18)	2.065(2)–2.256(2)	HS	[7]

a: spin crossover temperature; b: structure analyses temperature

Table S5: Spin crossover behaviors of [Mn(5Cl-sal$_2$-323)](Y) (Y = counteranion) complexes with associated Mn–N/O bond distances

Complex X	$T_{1/2}$ (K)[a]	T (K)[b]	Mn–O (Å)	Mn–N (Å)	Spin State	Ref.
[Mn(5Cl-sal$_2$-323)](BPh$_4$) **Y = BPh$_4$**	$T_{1/2}$ (1) = 168 K $T_{1/2}$ (2) = 103 K Two-step and complete	100 120 240	1.8753(13)-1.8661(13) 1.856(4)-1.864(4) 1.865(4)-1.861(4) 1.8650(19)-1.8540(19)	2.0742(18)-2.0808(16) 2.0005(17)-2.0085(17) 2.139(5)-2.121(5) 2.047(5)2.022(5) 2.098(5)-2.101(5) 2.005(5)-2.018(5) 2.167(3)-2.179(3) 2.060(2)-2.095(3)	LS HS]:[LS] (1:1) HS	This work
[Mn(5Cl-sal$_2$-323)](TCNQ)$_{1.5}$·2MeCN[c] **Y = TCNQ$_{1.5}$**	$T_{1/2}\downarrow$ = 73, $T_{1/2}\uparrow$ = 123; $\Delta T_{1/2}$ = 50 hysteretic and abrupt; One step and complete	100 220	1.872(2)–1.884(2) 1.871(2)–1.881(2)	2.089(3)–2.222(3) 2.095(2)–2.220(2)	HS HS	[8]
[Mn(5-Cl-Sal-323)](NO$_3$) **Y = NO$_3$**	~ 200 gradual and incomplete	100 293	1.8690(12)–1.8737(12) 1.8726(12)–1.8767(12) 1.876(2) 1.878(2)–1.879(2)	2.0695(14)–2.2613(14) 2.0628(15)–2.1929 (15) 2.091(2)–2.244(3) 2.100(3)–2.206(3)	HS HS	[9]
[Mn(5-Cl-Sal-323)]ClO$_4$ **Y = ClO$_4$**	>281 gradual and incomplete	100 260	1.8608(13) 1.8787(13) 1.8641(16)–1.8641(16) 1.8726(15)	2.1071(16)–2.2201(17) 1.9826(17)–2.0484 (18) 2.1055(19)–2.219(2)	[HS]:[LS] (1:1) HS	[9]

a: spin crossover temperature; b: structure analyses temperature; c: TCNQ = 7,7,8,8,-tetracyanoquinodimethane

Appendix: Check cif files for complex **1**.

Temperature: 240 K

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 240K

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 240K

```
Bond precision:  C-C = 0.0053 A          Wavelength=0.71073

Cell:           a=14.3566(10)    b=21.8039(15)      c=14.4656(11)
                alpha=90         beta=116.203(3)    gamma=90
Temperature:    240 K

                Calculated                Reported
Volume          4062.8(5)                 4062.8(5)
Space group     P 21/n                    P 1 21/n 1
Hall group      -P 2yn                    -P 2yn
Moiety formula  C24 H20 B, C22 H26 Cl2 Mn N4 O2  C22 H26 Cl2 Mn N4 O2, C24
                                          H20 B

Sum formula     C46 H46 B Cl2 Mn N4 O2    C46 H46 B Cl2 Mn N4 O2
Mr              823.52                    823.52
Dx,g cm-3       1.346                     1.346
Z               4                         4
Mu (mm-1)       0.501                     0.501
F000            1720.0                    1720.0
F000'           1723.06
h,k,lmax        17,25,17                  17,25,17
Nref            7143                      7143
Tmin,Tmax       0.897,0.937               0.651,0.746
Tmin'           0.810

Correction method= # Reported T Limits: Tmin=0.651 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 24.999

R(reflections)= 0.0456( 4763)     wR2(reflections)= 0.1148( 7143)

S = 1.014                 Npar= 738
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.128
PLAT088_ALERT_3_C Poor Data / Parameter Ratio .....................      9.68 Note
PLAT332_ALERT_2_C Large Phenyl C-C Range     C29       -C34B     .      0.18 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N1        --H1      .    Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N2        --H2      .    Please Check
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        10 Report
PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 .........     0.128 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ  Please Check
 PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct.         2 Note
 PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records         1 Report
 PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records         3 Report
 PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         2 Report
 PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )       96% Note
 PLAT793_ALERT_4_G Model has Chirality at N1          (Centro SPGR)        R Verify
 PLAT793_ALERT_4_G Model has Chirality at N2          (Centro SPGR)        R Verify
 PLAT794_ALERT_5_G Tentative Bond Valency for Mn1       (I)       .     0.85 Info
 PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....        ! Info
 PLAT860_ALERT_3_G Number of Least-Squares Restraints .............      423 Note
 PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .  Please Do !
 PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still      37% Note
 PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  16 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

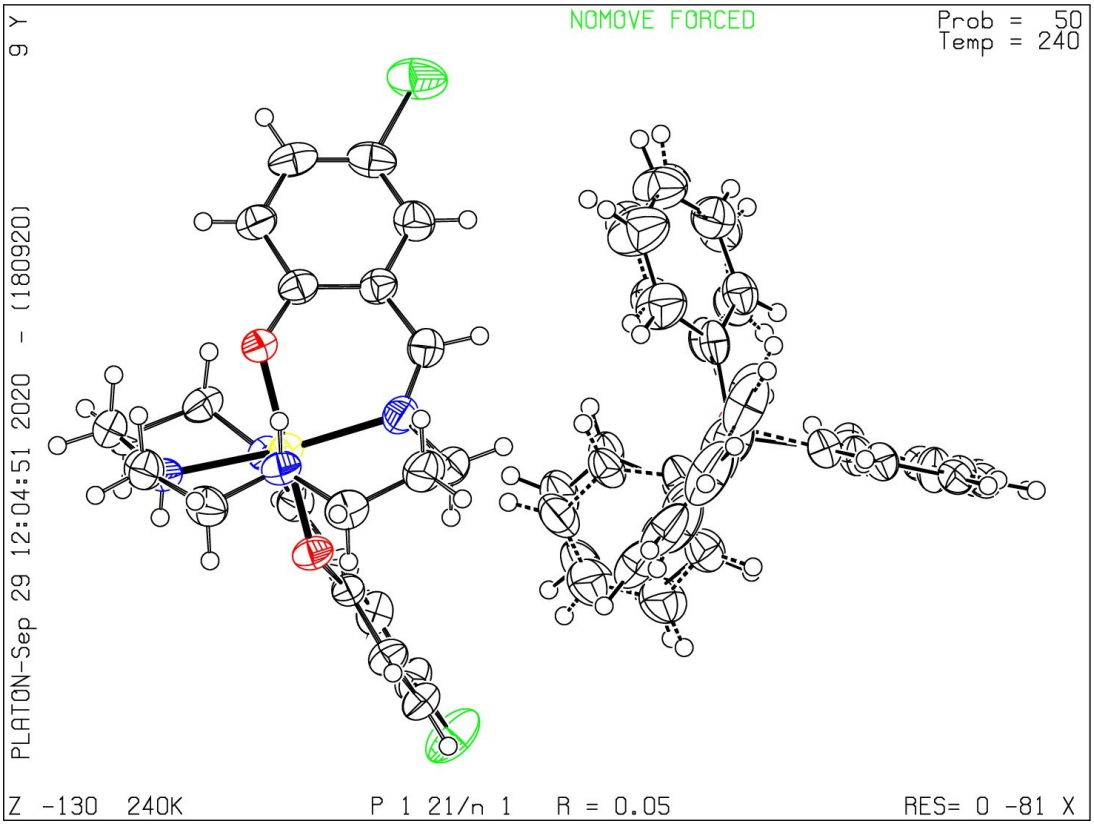
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/09/2020; check.def file version of 20/08/2020

Datablock 240K - ellipsoid plot



Temperature: 120K

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 120K

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 120K

```
Bond precision:  C-C = 0.0082 A          Wavelength=0.71073

Cell:           a=14.2615(10)    b=21.6350(14)      c=14.4098(10)
                alpha=90         beta=116.523(2)    gamma=90
Temperature:    120 K
```

	Calculated	Reported
Volume	3978.2(5)	3978.2(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C22 H26 Cl2 Mn N4 O2, C24 H20 B	C22 H26 Cl2 Mn N4 O2, 1(C24 H20 B1)
Sum formula	C46 H46 B Cl2 Mn N4 O2	C46 H46 B Cl2 Mn N4 O2
Mr	823.52	823.52
Dx,g cm-3	1.375	1.375
Z	4	4
Mu (mm-1)	0.511	0.511
F000	1720.0	1720.0
F000’	1723.06	
h,k,lmax	17,27,18	17,27,18
Nref	8237	8238
Tmin,Tmax	0.895,0.936	0.651,0.746
Tmin’	0.807	

```
Correction method= # Reported T Limits: Tmin=0.651 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 26.499

R(reflections)= 0.0768( 5405)     wR2(reflections)= 0.1648( 8238)

S = 1.128                 Npar= 731
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.136
PLAT020_ALERT_3_C The Value of Rint is Greater Than 0.12 .....      0.136 Report
PLAT332_ALERT_2_C Large Phenyl C-C Range     C29A      -C34A     .       0.18 Ang.
PLAT332_ALERT_2_C Large Phenyl C-C Range     C35A      -C40A     .       0.17 Ang.
PLAT332_ALERT_2_C Large Phenyl C-C Range     C29B      -C34B     .       0.25 Ang.
PLAT332_ALERT_2_C Large Phenyl C-C Range     C35B      -C40B     .       0.22 Ang.
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00816 Ang.
PLAT420_ALERT_2_C D-H Without Acceptor       N1       --H1       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N2       --H2       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     11.869 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.657 Check
PLAT977_ALERT_2_C Check Negative Difference Density on H25A            -0.31 eA-3
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          3 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      18.12 Why ?
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          3 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1      --N4       .        6.0 s.u.
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )      26.69 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  3  )      18.31 Check
PLAT793_ALERT_4_G Model has Chirality at N1          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at N2          (Centro SPGR)          R Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Mn1       (I)       .       0.91 Info
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        414 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  17 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  11 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   8 ALERT type 4 Improvement, methodology, query or suggestion
   3 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of apaper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

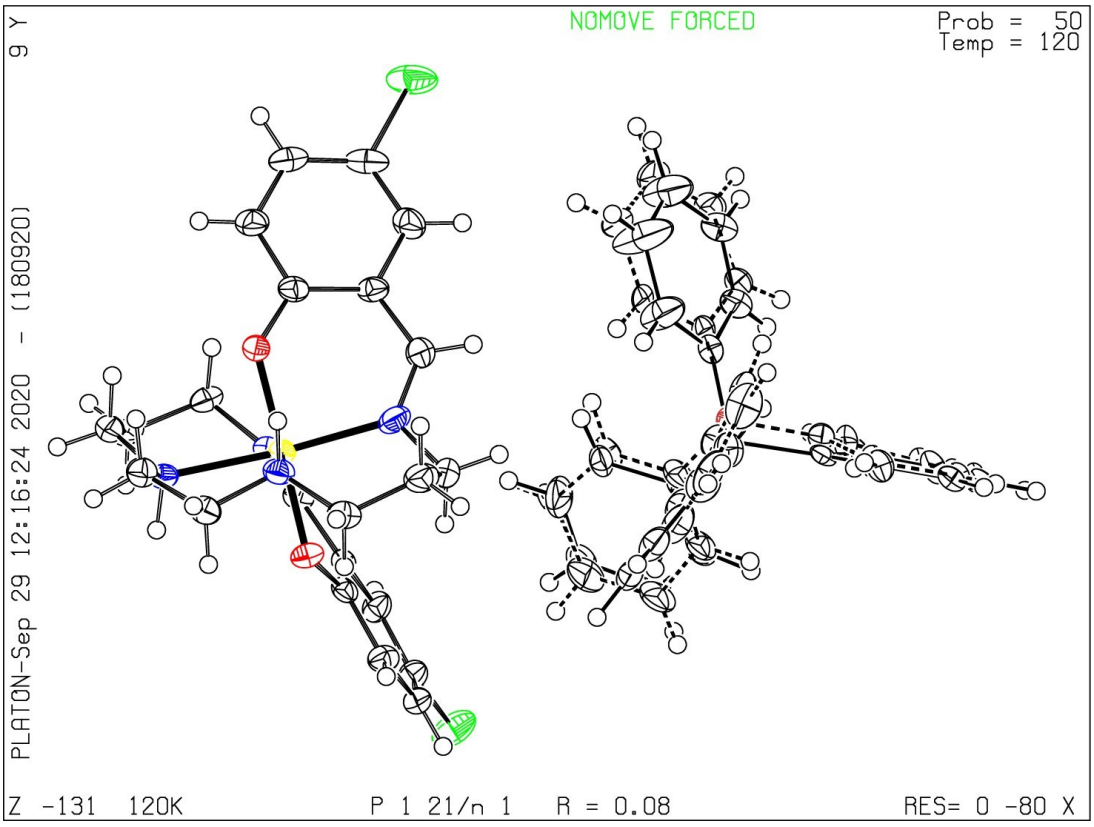
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/09/2020; check.def file version of 20/08/2020

Datablock 120K - ellipsoid plot



Temperature: 100 K

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 100K

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 100K

```
Bond precision:  C-C = 0.0024 A          Wavelength=0.71073

Cell:            a=14.2627(5)    b=21.6172(8)        c=14.4837(5)
                 alpha=90        beta=116.711(2)     gamma=90
Temperature:     100 K
```

	Calculated	Reported
Volume	3989.1(3)	3989.1(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2ybc (x-
Moiety formula	C22 H26 Cl2 Mn N4 O2, C24 H20 B	C22 H26 Cl2 Mn N4 O2, C24 H20 B
Sum formula	C46 H46 B Cl2 Mn N4 O2	C46 H46 B Cl2 Mn N4 O2
Mr	823.52	823.57
Dx,g cm-3	1.371	1.365
Z	4	4
Mu (mm-1)	0.510	0.510
F000	1720.0	1723.2
F000’	1723.06	
h,k,lmax	20,31,20	20,30,20
Nref	12432	12377
Tmin,Tmax	0.896,0.936	0.651,0.746
Tmin’	0.807	

```
Correction method= # Reported T Limits: Tmin=0.651 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 30.740

R(reflections)= 0.0438( 10956)    wR2(reflections)= 0.0976( 12377)

S = 1.054                 Npar= 747
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT126_ALERT_1_C Error in or Uninterpretable Hall Symbol  .......  -P 2YBC   (X-Z,Y
PLAT221_ALERT_2_C Solv./Anion  Resd 2  C   Ueq(max)/Ueq(min) Range       5.1 Ratio
PLAT223_ALERT_4_C Solv./Anion  Resd 2  H   Ueq(max)/Ueq(min) Range       5.1 Ratio
PLAT420_ALERT_2_C D-H Without Acceptor       N1       --H1       .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N2       --H2       .     Please Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     2.807 Check
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...        50 Report
PLAT068_ALERT_1_G Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large      5.57 Why ?
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct.         2 Note
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records         2 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records         2 Report
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1      --N1       .       9.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Mn1      --N4       .      10.3 s.u.
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT304_ALERT_4_G  Non-Integer  Number  of  Atoms  in  .....  (Resd  2  )  30.78  Check
PLAT304_ALERT_4_G  Non-Integer  Number  of  Atoms  in  .....  (Resd  3  )  14.22  Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  Cl1      ..C26B             3.25 Ang.
                                                -x,-y,1-z  =      3_556 Check
PLAT769_ALERT_4_G CIF Embedded explicitly supplied scattering data     Please Note
PLAT793_ALERT_4_G Model has Chirality at N1          (Centro SPGR)          R Verify
PLAT793_ALERT_4_G Model has Chirality at N2          (Centro SPGR)          R Verify
PLAT794_ALERT_5_G Tentative Bond Valency for Mn1       (I)       .      0.93 Info
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....         ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       444 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        50 Note
PLAT960_ALERT_3_G Number of Intensities with I  <   - 2*sig(I) ...         5 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        19 Info
 PLAT982_ALERT_1_G The Mn-f'=     0.3478 Deviates from   IT-value =      0.3368 Check
 PLAT983_ALERT_1_G The Cl-f"=     0.1603 Deviates from   IT-Value =      0.1585 Check
 PLAT983_ALERT_1_G The Mn-f"=     0.7326 Deviates from   IT-Value =      0.7283 Check
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  26 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   9 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
  12 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

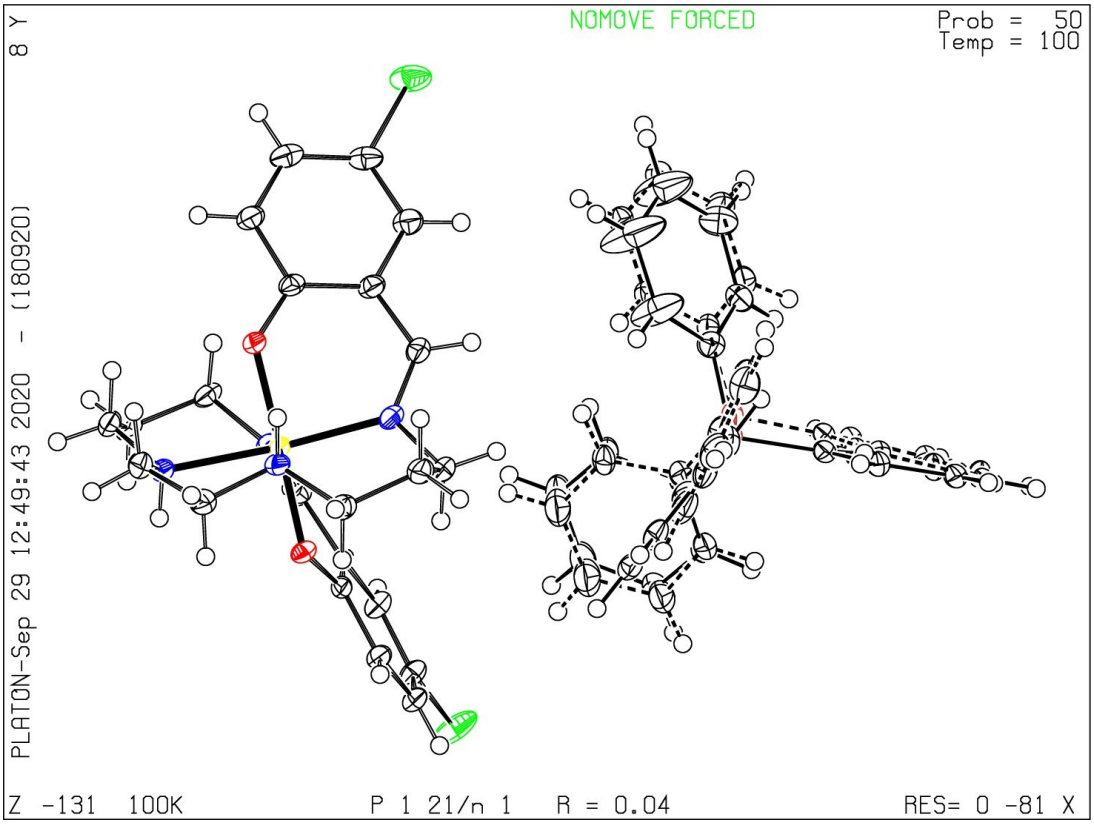
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/09/2020; check.def file version of 20/08/2020

Datablock 100K - ellipsoid plot


NOMOVE FORCED
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8 Y
PLATON-Sep 29 12:49:43 2020 - (180920)
Z -131 100K
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RES= 0 -81 X

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