Supplementary Material

Observation of Magnetic Ordering as high as 28 K for meso-tetrakis(4-halophenyl)porphyrinatomanganese(III) Tetracyanoethenide, [MnTXPP][TCNE] (X = F, Br, I)

Durrell K. Rittenberg and Joel S. Miller

Department of Chemistry, 315 S. 1400 E. RM Dock, University of Utah, Salt Lake City, Utah, 84112-0850

Table S1 Crystal data and structure refinement for **1Br,** [MnTBrPP][TCNE]·2PhMe.

Empirical formula	$C_{64}H_{40}Br_4MnN_8$	
Formula weight	1295.62 g/mol	
Temperature	200(2) K	
Wavelength	0.71070 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0790(3) Å	α= 73.1830(15)°.
	b = 10.2770(2) Å	β= 84.3080(11)°.
	c = 14.6260(4) Å	γ = 68.9920(15)°.
Volume	1353.79(6) $Å^3$	
Z	1	
Density (calculated)	1.589 mg/cm^3	
Absorption coefficient	3.246 mm^{-1}	
F(000)	645	
Crystal size	0.25 x 0.25 x 0.20 mm^3	
Theta range for data collection	2.16 to 24.79°.	
Index ranges	0<=h<=11, -10<=k<=12, -16<=l<=17	
Reflections collected	4563	
Independent reflections	4563 [R(int) = 0.0000]	
Completeness to theta = 24.79°	98.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4563 / 0 / 366	
Goodness-of-fit on F^2	1.145	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1192	
R indices (all data)	R1 = 0.0514, wR2 = 0.1474	
Largest diff. peak and hole	1.140 and -1.216 e/$Å^3$	

Table S2. Atomic coordinates ,x 10^4, and equivalent isotropic displacement parameters, $Å^2$x 10^3, for **1Br,** [MnTBrPP][TCNE]·2PhMe. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	10000	0	5000	18(1)
Br(1)	6541(1)	3757(1)	-1487(1)	60(1)
Br(2)	629(1)	3369(1)	7508(1)	49(1)
C(1)	10565(4)	3161(4)	4804(3)	26(1)
C(2)	10584(4)	4524(4)	4807(3)	25(1)
C(3)	11757(4)	4935(4)	4401(3)	29(1)
C(4)	6826(4)	1735(4)	4815(3)	24(1)
C(5)	5717(4)	2501(4)	4122(3)	30(1)
C(6)	6297(4)	2466(4)	3255(3)	30(1)
C(7)	7786(4)	1651(4)	3402(3)	25(1)
C(8)	8749(4)	1300(4)	2672(3)	25(1)
C(9)	10180(4)	418(4)	2841(3)	24(1)
C(10)	11181(4)	74(4)	2109(3)	29(1)
C(11)	12463(4)	-706(4)	2536(3)	29(1)
C(12)	7729(4)	860(4)	6463(3)	23(1)
C(13)	6637(4)	1549(4)	5789(3)	24(1)
C(14)	8211(4)	1886(4)	1664(3)	26(1)
C(15)	7663(4)	3377(4)	1247(3)	30(1)
C(16)	7151(5)	3943(4)	316(3)	34(1)
C(17)	7208(5)	2993(5)	-205(3)	36(1)
C(18)	7740(5)	1515(4)	184(3)	36(1)
C(19)	8232(4)	963(4)	1119(3)	32(1)
C(20)	5155(4)	2077(4)	6159(3)	26(1)
C(21)	4598(4)	3351(4)	6418(3)	35(1)
C(22)	3244(4)	3765(5)	6809(3)	40(1)
C(23)	2464(4)	2868(5)	6941(3)	33(1)
C(24)	2973(4)	1615(5)	6668(3)	40(1)
C(25)	4318(4)	1214(4)	6274(3)	36(1)
C(26)	2518(6)	2826(6)	2602(4)	55(1)
C(27)	2632(5)	2700(5)	1596(3)	40(1)
C(28)	3925(5)	1993(5)	1225(4)	46(1)

C(29)	4008(6)	1798(6)	322(4)	53(1)
C(30)	2810(6)	2331(6)	-237(4)	55(1)
C(31)	1517(6)	3069(6)	113(4)	54(1)
C(32)	1442(5)	3251(5)	1009(4)	46(1)
N(1)	10523(3)	2057(3)	4816(3)	31(1)
N(2)	12686(4)	5293(4)	4063(3)	46(1)
N(3)	8107(3)	1212(3)	4360(2)	21(1)
N(4)	9152(3)	174(3)	6280(2)	22(1)

Table S3. Bond lengths, Å, and angles, °, for **1Br**, [MnTBrPP][TCNE]·2PhMe

Mn(1)-N(4)#1	2.009(3)
Mn(1)-N(4)	2.009(3)
Mn(1)-N(3)#1	2.011(3)
Mn(1)-N(3)	2.011(3)
Mn(1)-N(1)#1	2.293(3)
Mn(1)-N(1)	2.293(3)
Br(1)-C(17)	1.898(4)
Br(2)-C(23)	1.905(4)
C(1)-N(1)	1.145(5)
C(1)-C(2)	1.409(5)
C(2)-C(3)	1.416(5)
C(2)-C(2)#2	1.423(7)
C(3)-N(2)	1.143(5)
C(4)-C(13)	1.384(5)
C(4)-N(3)	1.392(5)
C(4)-C(5)	1.424(5)
C(5)-C(6)	1.348(6)
C(5)-H(5)	0.9300
C(6)-C(7)	1.435(5)
C(6)-H(6)	0.9300
C(7)-N(3)	1.376(5)
C(7)-C(8)	1.406(5)
C(8)-C(9)	1.403(5)
C(8)-C(14)	1.497(5)
C(9)-N(4)#1	1.379(5)
C(9)-C(10)	1.428(5)
C(10)-C(11)	1.353(6)
C(10)-H(10)	0.9300
C(11)-C(12)#1	1.428(5)
C(11)-H(11)	0.9300
C(12)-N(4)	1.391(4)
C(12)-C(13)	1.391(5)
C(12)-C(11)#1	1.428(5)
C(13)-C(20)	1.499(5)

C(14)-C(15)	1.394(5)
C(14)-C(19)	1.398(5)
C(15)-C(16)	1.387(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.384(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.377(6)
C(18)-C(19)	1.386(6)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-C(21)	1.374(5)
C(20)-C(25)	1.396(5)
C(21)-C(22)	1.393(6)
C(21)-H(21)	0.9300
C(22)-C(23)	1.376(6)
C(22)-H(22)	0.9300
C(23)-C(24)	1.366(6)
C(24)-C(25)	1.386(6)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9597
C(26)-C(27)	1.503(7)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-C(28)	1.389(7)
C(27)-C(32)	1.390(7)
C(28)-C(29)	1.382(8)
C(28)-H(28)	0.9300
C(29)-C(30)	1.374(8)
C(29)-H(29)	0.9300
C(30)-C(31)	1.386(8)
C(30)-H(30)	0.9300
C(31)-C(32)	1.368(8)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
N(4)-C(9)#1	1.379(5)

N(4)#1-Mn(1)-N(4)	180.000(2)
N(4)#1-Mn(1)-N(3)#1	90.71(12)
N(4)-Mn(1)-N(3)#1	89.29(12)
N(4)#1-Mn(1)-N(3)	89.29(12)
N(4)-Mn(1)-N(3)	90.71(12)
N(3)#1-Mn(1)-N(3)	180.00(16)
N(4)#1-Mn(1)-N(1)#1	89.23(12)
N(4)-Mn(1)-N(1)#1	90.77(12)
N(3)#1-Mn(1)-N(1)#1	89.99(12)
N(3)-Mn(1)-N(1)#1	90.01(12)
N(4)#1-Mn(1)-N(1)	90.77(12)
N(4)-Mn(1)-N(1)	89.23(12)
N(3)#1-Mn(1)-N(1)	90.01(12)
N(3)-Mn(1)-N(1)	89.99(12)
N(1)#1-Mn(1)-N(1)	180.0
N(1)-C(1)-C(2)	178.3(4)
C(1)-C(2)-C(3)	119.0(3)
C(1)-C(2)-C(2)#2	119.9(4)
C(3)-C(2)-C(2)#2	121.1(4)
N(2)-C(3)-C(2)	178.6(5)
C(13)-C(4)-N(3)	126.0(3)
C(13)-C(4)-C(5)	124.5(3)
N(3)-C(4)-C(5)	109.5(3)
C(6)-C(5)-C(4)	107.8(3)
C(6)-C(5)-H(5)	126.1
C(4)-C(5)-H(5)	126.1
C(5)-C(6)-C(7)	107.1(3)
C(5)-C(6)-H(6)	126.4
C(7)-C(6)-H(6)	126.4
N(3)-C(7)-C(8)	125.6(3)
N(3)-C(7)-C(6)	109.9(3)
C(8)-C(7)-C(6)	124.5(4)
C(9)-C(8)-C(7)	123.4(3)
C(9)-C(8)-C(14)	118.5(3)
C(7)-C(8)-C(14)	118.2(3)
N(4)#1-C(9)-C(8)	125.7(3)

N(4)#1-C(9)-C(10)	110.0(3)
C(8)-C(9)-C(10)	124.2(3)
C(11)-C(10)-C(9)	107.3(3)
C(11)-C(10)-H(10)	126.3
C(9)-C(10)-H(10)	126.3
C(10)-C(11)-C(12)#1	107.5(3)
C(10)-C(11)-H(11)	126.3
C(12)#1-C(11)-H(11)	126.3
N(4)-C(12)-C(13)	125.9(3)
N(4)-C(12)-C(11)#1	109.5(3)
C(13)-C(12)-C(11)#1	124.5(3)
C(4)-C(13)-C(12)	124.6(3)
C(4)-C(13)-C(20)	118.5(3)
C(12)-C(13)-C(20)	116.9(3)
C(15)-C(14)-C(19)	118.3(4)
C(15)-C(14)-C(8)	120.5(3)
C(19)-C(14)-C(8)	121.3(3)
C(16)-C(15)-C(14)	121.4(4)
C(16)-C(15)-H(15)	119.3
C(14)-C(15)-H(15)	119.3
C(17)-C(16)-C(15)	118.7(4)
C(17)-C(16)-H(16)	120.7
C(15)-C(16)-H(16)	120.7
C(18)-C(17)-C(16)	121.6(4)
C(18)-C(17)-Br(1)	119.5(3)
C(16)-C(17)-Br(1)	118.9(3)
C(17)-C(18)-C(19)	119.2(4)
C(17)-C(18)-H(18)	120.4
C(19)-C(18)-H(18)	120.4
C(18)-C(19)-C(14)	120.9(4)
C(18)-C(19)-H(19)	119.5
C(14)-C(19)-H(19)	119.5
C(21)-C(20)-C(25)	118.5(3)
C(21)-C(20)-C(13)	123.0(3)
C(25)-C(20)-C(13)	118.5(3)
C(20)-C(21)-C(22)	121.3(4)

C(20)-C(21)-H(21)	119.4
C(22)-C(21)-H(21)	119.4
C(23)-C(22)-C(21)	118.8(4)
C(23)-C(22)-H(22)	120.6
C(21)-C(22)-H(22)	120.6
C(24)-C(23)-C(22)	121.3(4)
C(24)-C(23)-Br(2)	118.7(3)
C(22)-C(23)-Br(2)	120.1(3)
C(23)-C(24)-C(25)	119.6(4)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(24)-C(25)-C(20)	120.5(4)
C(24)-C(25)-H(25)	120.6
C(20)-C(25)-H(25)	118.8
C(27)-C(26)-H(26A)	109.5
C(27)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(27)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(28)-C(27)-C(32)	117.3(5)
C(28)-C(27)-C(26)	121.3(5)
C(32)-C(27)-C(26)	121.3(5)
C(29)-C(28)-C(27)	121.0(5)
C(29)-C(28)-H(28)	119.5
C(27)-C(28)-H(28)	119.5
C(30)-C(29)-C(28)	120.4(5)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(29)-C(30)-C(31)	119.3(5)
C(29)-C(30)-H(30)	120.4
C(31)-C(30)-H(30)	120.4
C(32)-C(31)-C(30)	119.9(5)
C(32)-C(31)-H(31)	120.0
C(30)-C(31)-H(31)	120.0
C(31)-C(32)-C(27)	122.0(5)

C(31)-C(32)-H(32)	119.0
C(27)-C(32)-H(32)	119.0
C(1)-N(1)-Mn(1)	168.1(3)
C(7)-N(3)-C(4)	105.7(3)
C(7)-N(3)-Mn(1)	128.1(2)
C(4)-N(3)-Mn(1)	126.2(2)
C(9)#1-N(4)-C(12)	105.7(3)
C(9)#1-N(4)-Mn(1)	128.0(2)
C(12)-N(4)-Mn(1)	126.3(2)

Symmetry transformations used to generate equivalent atoms:

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

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	14(1)	15(1)	25(1)	-7(1)	3(1)	-3(1)
Br(1)	96(1)	44(1)	34(1)	-7(1)	-21(1)	-13(1)
Br(2)	19(1)	70(1)	38(1)	-6(1)	7(1)	-1(1)
C(1)	24(2)	24(2)	29(2)	-8(2)	2(2)	-8(2)
C(2)	24(2)	18(2)	32(2)	-7(1)	-2(2)	-7(1)
C(3)	23(2)	22(2)	41(2)	-12(2)	2(2)	-6(2)
C(4)	17(2)	22(2)	33(2)	-10(2)	1(2)	-5(1)
C(5)	16(2)	33(2)	36(2)	-10(2)	2(2)	-4(2)
C(6)	17(2)	31(2)	36(2)	-10(2)	-5(2)	0(2)
C(7)	21(2)	21(2)	32(2)	-8(2)	0(2)	-5(1)
C(8)	21(2)	23(2)	31(2)	-11(2)	2(2)	-5(1)
C(9)	22(2)	21(2)	28(2)	-9(1)	3(2)	-5(1)
C(10)	25(2)	30(2)	29(2)	-9(2)	4(2)	-6(2)
C(11)	23(2)	28(2)	32(2)	-12(2)	6(2)	-4(2)
C(12)	18(2)	17(2)	35(2)	-10(1)	5(2)	-6(1)
C(13)	18(2)	18(2)	34(2)	-10(1)	3(2)	-4(1)
C(14)	19(2)	27(2)	30(2)	-9(2)	1(2)	-4(2)
C(15)	28(2)	29(2)	32(2)	-11(2)	1(2)	-8(2)
C(16)	36(2)	27(2)	34(2)	-8(2)	1(2)	-7(2)
C(17)	40(2)	37(2)	27(2)	-8(2)	-2(2)	-10(2)
C(18)	40(2)	32(2)	35(2)	-15(2)	-3(2)	-7(2)
C(19)	33(2)	25(2)	34(2)	-9(2)	-1(2)	-6(2)
C(20)	17(2)	27(2)	29(2)	-7(2)	1(2)	-4(1)
C(21)	23(2)	35(2)	51(3)	-22(2)	10(2)	-10(2)
C(22)	28(2)	39(2)	53(3)	-25(2)	7(2)	-5(2)
C(23)	16(2)	44(2)	29(2)	-5(2)	1(2)	-1(2)
C(24)	25(2)	43(2)	51(3)	-11(2)	8(2)	-17(2)
C(25)	28(2)	31(2)	51(3)	-16(2)	7(2)	-11(2)
C(26)	58(3)	54(3)	53(3)	-15(2)	6(2)	-21(3)
C(27)	40(2)	31(2)	49(3)	-9(2)	0(2)	-15(2)
C(28)	34(3)	42(3)	61(3)	-13(2)	-7(2)	-10(2)

C(29)	45(3)	53(3)	63(3)	-26(3)	8(2)	-14(2)
C(30)	65(4)	57(3)	50(3)	-18(2)	-2(3)	-25(3)
C(31)	49(3)	54(3)	55(3)	-4(2)	-11(2)	-20(2)
C(32)	32(2)	42(2)	57(3)	-4(2)	0(2)	-11(2)
N(1)	29(2)	22(2)	45(2)	-14(1)	7(2)	-11(1)
N(2)	26(2)	34(2)	77(3)	-14(2)	9(2)	-12(2)
N(3)	17(1)	19(1)	28(2)	-10(1)	4(1)	-4(1)
N(4)	18(2)	18(1)	29(2)	-8(1)	4(1)	-4(1)

Hydrogen coordinates, $x10^4$, and equivalent isotropic displacement parameters, $Å^2 x10^3$ for **1Br**, [MnTBrPP][TCNE]·2PhMe

Table S6. Crystal data and structure refinement for **1I**, [MnTIPP][TCNE]·2PhMe.

Identification code	[MnTIPP][TCNE]·2PhMe, 1I	
Empirical formula	$C_{64}H_{40}I_4MnN_8$	
Formula weight	1483.58	
Temperature	200(0.1)K	
Wavelength	0.71070 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8305(2) Å	α= 81.0748(17)°.
	b = 10.1012(3) Å	β= 79.6338(18)°.
	c = 15.3990(6) Å	γ = 72.7559(18)°.
Volume	1428.09(8) $Å^3$	
Z	1	
Density (calculated)	1.725 Mg/m^3	
Absorption coefficient	2.441 mm^{-1}	
F(000)	717	
Crystal size	0.20 x 0.18 x 0.005 mm^3	
Theta range for data collection	2.60 to 24.72°.	
Index ranges	0<=h<=11, -10<=k<=11, -17<=l<=18	
Reflections collected	4832	
Independent reflections	4832 [R(int) = 0.0000]	
Completeness to theta = 24.72°	99.1 %	
Absorption correction	Scalepack	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4832 / 4 / 337	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0929	
R indices (all data)	R1 = 0.0516, wR2 = 0.1008	
Largest diff. peak and hole	1.140 and -0.859 $e.Å^{-3}$	

Table S7. Atomic coordinates, x 10^4, and equivalent isotropic displacement parameters, $Å^2$x 10^3, for **1I**, [MnTIPP][TCNE]·2PhMe.. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn	10000	5000	10000	25(1)
I(1)	18973(1)	820(1)	12533(1)	51(1)
I(2)	14920(1)	2120(1)	4173(1)	74(1)
N(1)	9292(4)	3017(4)	10138(3)	38(1)
N(2)	7349(5)	30(5)	9313(5)	77(2)
N(3)	10529(4)	4603(4)	11236(2)	29(1)
N(4)	11996(4)	3922(4)	9522(2)	28(1)
C(1)	9305(4)	1934(5)	10016(3)	32(1)
C(2)	9397(5)	546(5)	9896(3)	35(1)
C(3)	8256(5)	286(5)	9570(4)	46(1)
C(4)	11855(4)	3867(5)	11481(3)	33(1)
C(5)	13091(4)	3293(4)	10903(3)	32(1)
C(6)	13131(4)	3289(4)	9996(3)	31(1)
C(7)	14354(5)	2592(5)	9426(3)	38(1)
C(8)	13972(5)	2783(5)	8610(3)	37(1)
C(9)	12518(4)	3630(4)	8652(3)	29(1)
C(10)	11751(4)	4120(5)	7934(3)	31(1)
C(11)	10340(4)	4967(5)	7993(3)	31(1)
C(12)	9566(5)	5507(5)	7261(3)	41(1)
C(13)	8220(5)	6205(5)	7580(3)	40(1)
C(14)	14469(4)	2670(4)	11294(3)	31(1)
C(15)	15237(5)	3550(5)	11433(4)	42(1)
C(16)	16518(5)	3016(5)	11786(4)	41(1)
C(17)	17027(4)	1609(5)	11999(3)	34(1)
C(18)	16286(5)	728(5)	11862(4)	48(1)
C(19)	15010(5)	1255(5)	11504(4)	49(1)
C(20)	12495(4)	3662(5)	7046(3)	35(1)
C(21)	13704(5)	4060(6)	6625(4)	44(1)
C(22)	14417(5)	3607(6)	5810(4)	50(1)
C(23)	13878(5)	2764(6)	5416(3)	46(1)
C(24)	12682(6)	2348(6)	5820(4)	50(1)

C(25)	11988(5)	2803(6)	6631(3)	44(1)
C(26)	21278(15)	-3390(20)	15021(15)	306(17)
C(27)	21612(7)	-2604(13)	14461(8)	157(6)
C(28)	21699(7)	-1282(14)	14544(7)	134(5)
C(29)	22132(9)	-455(9)	13800(12)	211(10)
C(30)	22477(7)	-949(17)	12972(8)	235(13)
C(31)	22390(8)	-2271(19)	12888(7)	230(13)
C(32)	21957(9)	-3098(11)	13632(11)	216(11)

Table S8. Bond lengths, Å, and angles, °, for **1I**, [MnTIPP][TCNE]·2PhMe.

Mn-N(4)	2.010(3)
Mn-N(4)#1	2.010(3)
Mn-N(3)	2.013(4)
Mn-N(3)#1	2.013(4)
Mn-N(1)	2.276(4)
Mn-N(1)#1	2.276(4)
I(1)-C(17)	2.104(4)
I(2)-C(23)	2.102(5)
N(1)-C(1)	1.134(6)
N(2)-C(3)	1.146(7)
N(3)-C(11)#1	1.379(6)
N(3)-C(4)	1.382(5)
N(4)-C(6)	1.382(5)
N(4)-C(9)	1.389(6)
C(1)-C(2)	1.416(7)
C(2)-C(2)#2	1.405(9)
C(2)-C(3)	1.414(7)
C(4)-C(5)	1.399(6)
C(4)-C(13)#1	1.425(7)
C(5)-C(6)	1.391(6)
C(5)-C(14)	1.504(6)
C(6)-C(7)	1.421(6)
C(7)-C(8)	1.346(7)
C(7)-H(7)	0.9300
C(8)-C(9)	1.427(6)
C(8)-H(8)	0.9300
C(9)-C(10)	1.396(6)
C(10)-C(11)	1.392(6)
C(10)-C(20)	1.501(6)
C(11)-N(3)#1	1.379(6)
C(11)-C(12)	1.421(6)
C(12)-C(13)	1.345(7)
C(12)-H(12)	0.9300
C(13)-C(4)#1	1.425(7)

C(13)-H(13)	0.9300
C(14)-C(19)	1.378(7)
C(14)-C(15)	1.386(7)
C(15)-C(16)	1.387(7)
C(15)-H(15)	0.9300
C(16)-C(17)	1.367(7)
C(16)-H(16)	0.9300
C(17)-C(18)	1.366(7)
C(18)-C(19)	1.386(7)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-C(21)	1.386(7)
C(20)-C(25)	1.398(7)
C(21)-C(22)	1.396(7)
C(21)-H(21)	0.9300
C(22)-C(23)	1.385(8)
C(22)-H(22)	0.9300
C(23)-C(24)	1.376(8)
C(24)-C(25)	1.385(7)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-C(27)	1.148(14)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-C(28)	1.3900
C(27)-C(32)	1.3900
C(28)-C(29)	1.3900
C(28)-H(28)	0.9300
C(29)-C(30)	1.3900
C(29)-H(29)	0.9300
C(30)-C(31)	1.3900
C(30)-H(30)	0.9300
C(31)-C(32)	1.3900
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300

N(4)-Mn-N(4)#1	180.000(1)
N(4)-Mn-N(3)	90.25(14)
N(4)#1-Mn-N(3)	89.75(14)
N(4)-Mn-N(3)#1	89.75(14)
N(4)#1-Mn-N(3)#1	90.25(14)
N(3)-Mn-N(3)#1	180.000(1)
N(4)-Mn-N(1)	89.01(14)
N(4)#1-Mn-N(1)	90.99(14)
N(3)-Mn-N(1)	92.55(15)
N(3)#1-Mn-N(1)	87.45(15)
N(4)-Mn-N(1)#1	90.99(14)
N(4)#1-Mn-N(1)#1	89.01(14)
N(3)-Mn-N(1)#1	87.45(15)
N(3)#1-Mn-N(1)#1	92.55(15)
N(1)-Mn-N(1)#1	180.000(1)
C(1)-N(1)-Mn	158.7(4)
C(11)#1-N(3)-C(4)	106.0(4)
C(11)#1-N(3)-Mn	127.3(3)
C(4)-N(3)-Mn	126.7(3)
C(6)-N(4)-C(9)	105.5(3)
C(6)-N(4)-Mn	127.1(3)
C(9)-N(4)-Mn	127.4(3)
N(1)-C(1)-C(2)	176.2(5)
C(2)#2-C(2)-C(3)	121.0(5)
C(2)#2-C(2)-C(1)	120.2(5)
C(3)-C(2)-C(1)	118.8(4)
N(2)-C(3)-C(2)	177.8(6)
N(3)-C(4)-C(5)	125.7(4)
N(3)-C(4)-C(13)#1	109.4(4)
C(5)-C(4)-C(13)#1	124.9(4)
C(6)-C(5)-C(4)	124.4(4)
C(6)-C(5)-C(14)	118.4(4)
C(4)-C(5)-C(14)	117.2(4)
N(4)-C(6)-C(5)	125.6(4)
N(4)-C(6)-C(7)	110.2(4)

C(5)-C(6)-C(7)	124.2(4)
C(8)-C(7)-C(6)	107.1(4)
C(8)-C(7)-H(7)	126.5
C(6)-C(7)-H(7)	126.5
C(7)-C(8)-C(9)	108.1(4)
C(7)-C(8)-H(8)	126.0
C(9)-C(8)-H(8)	126.0
N(4)-C(9)-C(10)	125.2(4)
N(4)-C(9)-C(8)	109.1(4)
C(10)-C(9)-C(8)	125.7(4)
C(11)-C(10)-C(9)	124.4(4)
C(11)-C(10)-C(20)	118.5(4)
C(9)-C(10)-C(20)	117.2(4)
N(3)#1-C(11)-C(10)	125.8(4)
N(3)#1-C(11)-C(12)	109.4(4)
C(10)-C(11)-C(12)	124.7(4)
C(13)-C(12)-C(11)	107.8(4)
C(13)-C(12)-H(12)	126.1
C(11)-C(12)-H(12)	126.1
C(12)-C(13)-C(4)#1	107.3(4)
C(12)-C(13)-H(13)	126.3
C(4)#1-C(13)-H(13)	126.3
C(19)-C(14)-C(15)	118.7(4)
C(19)-C(14)-C(5)	122.5(4)
C(15)-C(14)-C(5)	118.8(4)
C(14)-C(15)-C(16)	120.6(4)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(17)-C(16)-C(15)	119.7(4)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
C(18)-C(17)-C(16)	120.4(4)
C(18)-C(17)-I(1)	120.5(3)
C(16)-C(17)-I(1)	119.2(3)
C(17)-C(18)-C(19)	120.2(5)
C(17)-C(18)-H(18)	119.9

C(19)-C(18)-H(18)	119.9
C(14)-C(19)-C(18)	120.4(5)
C(14)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(21)-C(20)-C(25)	118.5(4)
C(21)-C(20)-C(10)	121.2(4)
C(25)-C(20)-C(10)	120.3(4)
C(20)-C(21)-C(22)	121.2(5)
C(20)-C(21)-H(21)	119.4
C(22)-C(21)-H(21)	119.4
C(23)-C(22)-C(21)	118.7(5)
C(23)-C(22)-H(22)	120.7
C(21)-C(22)-H(22)	120.7
C(24)-C(23)-C(22)	121.3(5)
C(24)-C(23)-I(2)	119.9(4)
C(22)-C(23)-I(2)	118.7(4)
C(23)-C(24)-C(25)	119.4(5)
C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3
C(24)-C(25)-C(20)	120.9(5)
C(24)-C(25)-H(25)	119.5
C(20)-C(25)-H(25)	119.5
C(27)-C(26)-H(26A)	109.5
C(27)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(27)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(26)-C(27)-C(28)	126.7(18)
C(26)-C(27)-C(32)	113.3(18)
C(28)-C(27)-C(32)	120.0
C(29)-C(28)-C(27)	120.0
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(28)-C(29)-C(30)	120.0
C(28)-C(29)-H(29)	120.0

C(30)-C(29)-H(29)	120.0
C(31)-C(30)-C(29)	120.0
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-H(30)	120.0
C(30)-C(31)-C(32)	120.0
C(30)-C(31)-H(31)	120.0
C(32)-C(31)-H(31)	120.0
C(31)-C(32)-C(27)	120.0
C(31)-C(32)-H(32)	120.0
C(27)-C(32)-H(32)	120.0

Symmetry transformations used to generate equivalent atoms:

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

Table S9. Anisotropic displacement parameters, $Å^2 x\ 10^3$, for **1I**, [MnTIPP][TCNE]·2PhMe. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn	20(1)	24(1)	31(1)	-7(1)	-7(1)	-1(1)
I(1)	30(1)	72(1)	51(1)	-7(1)	-18(1)	-6(1)
I(2)	54(1)	118(1)	34(1)	-23(1)	1(1)	3(1)
N(1)	33(2)	29(2)	53(3)	-10(2)	-6(2)	-10(2)
N(2)	43(3)	61(3)	138(6)	-45(3)	-37(3)	0(2)
N(3)	21(2)	31(2)	34(2)	-7(2)	-7(2)	0(1)
N(4)	25(2)	27(2)	32(2)	-5(2)	-8(2)	-3(1)
C(1)	23(2)	38(3)	33(3)	-9(2)	-1(2)	-6(2)
C(2)	30(2)	30(2)	46(3)	-12(2)	-4(2)	-7(2)
C(3)	35(3)	32(3)	74(4)	-18(3)	-14(3)	-1(2)
C(4)	25(2)	33(2)	38(3)	-5(2)	-9(2)	-3(2)
C(5)	26(2)	29(2)	39(3)	-3(2)	-9(2)	-4(2)
C(6)	25(2)	28(2)	39(3)	-5(2)	-10(2)	-2(2)
C(7)	26(2)	42(3)	41(3)	-11(2)	-5(2)	2(2)
C(8)	28(2)	41(3)	39(3)	-13(2)	-2(2)	0(2)
C(9)	24(2)	30(2)	34(3)	-6(2)	-3(2)	-7(2)
C(10)	27(2)	33(2)	33(3)	-7(2)	-2(2)	-6(2)
C(11)	27(2)	35(2)	30(2)	-4(2)	-6(2)	-8(2)
C(12)	30(2)	56(3)	31(3)	-6(2)	-7(2)	-2(2)
C(13)	31(2)	52(3)	33(3)	-5(2)	-11(2)	-1(2)
C(14)	24(2)	35(2)	33(3)	-6(2)	-6(2)	-4(2)
C(15)	33(2)	34(3)	57(3)	-4(2)	-11(2)	-4(2)
C(16)	32(2)	44(3)	54(3)	-15(2)	-9(2)	-14(2)
C(17)	25(2)	46(3)	29(2)	-10(2)	-6(2)	-3(2)
C(18)	40(3)	33(3)	74(4)	1(3)	-28(3)	-5(2)
C(19)	41(3)	39(3)	74(4)	-3(3)	-30(3)	-10(2)
C(20)	24(2)	42(3)	33(3)	-7(2)	-6(2)	0(2)
C(21)	32(3)	53(3)	46(3)	-10(2)	-2(2)	-10(2)
C(22)	34(3)	71(4)	38(3)	-3(3)	1(2)	-10(3)
C(23)	34(3)	65(3)	27(3)	-9(2)	-2(2)	5(2)
C(24)	44(3)	67(4)	41(3)	-20(3)	-4(2)	-11(3)

C(25)	35(3)	56(3)	41(3)	-14(2)	-1(2)	-12(2)
C(26)	138(13)	380(30)	350(30)	260(30)	-109(16)	-94(16)
C(27)	49(5)	208(16)	206(18)	-2(13)	-24(7)	-33(8)
C(28)	63(6)	201(13)	144(11)	-82(11)	-36(7)	1(7)
C(29)	49(6)	420(30)	138(12)	-78(17)	-41(7)	22(10)
C(30)	48(6)	400(40)	190(20)	63(19)	-40(10)	-6(12)
C(31)	36(7)	420(40)	210(20)	-100(20)	-27(9)	24(11)
C(32)	47(6)	390(30)	240(20)	-230(20)	-46(9)	11(9)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters, $Å^2$x 10^3, for **1I**, [MnTIPP][TCNE]·2PhMe.

	x	y	z	U(eq)
H(7)	15249	2098	9588	45
H(8)	14554	2425	8106	45
H(12)	9926	5396	6668	49
H(13)	7476	6652	7249	48
H(15)	14891	4506	11289	51
H(16)	17029	3612	11876	49
H(18)	16639	-228	12008	58
H(19)	14516	649	11406	59
H(21)	14047	4640	6890	53
H(22)	15238	3866	5536	60
H(24)	12343	1769	5552	61
H(25)	11173	2532	6902	53
H(26A)	21307	-4217	14780	459
H(26B)	20318	-2981	15300	459
H(26C)	21929	-3617	15453	459
H(28)	21468	-952	15098	161
H(29)	22190	430	13856	253
H(30)	22767	-395	12473	282
H(31)	22621	-2602	12334	276
H(32)	21899	-3983	13577	260

Table 6. Torsion angles [°] for [MnTIPP][TCNE]·2PhMe, 1I.

N(4)-Mn-N(1)-C(1)	-22.1(11)
N(4)#1-Mn-N(1)-C(1)	157.9(11)
N(3)-Mn-N(1)-C(1)	-112.3(11)
N(3)#1-Mn-N(1)-C(1)	67.7(11)
N(1)#1-Mn-N(1)-C(1)	74(100)
N(4)-Mn-N(3)-C(11)#1	179.7(4)
N(4)#1-Mn-N(3)-C(11)#1	-0.3(4)
N(3)#1-Mn-N(3)-C(11)#1	-8(100)
N(1)-Mn-N(3)-C(11)#1	-91.3(4)
N(1)#1-Mn-N(3)-C(11)#1	88.7(4)
N(4)-Mn-N(3)-C(4)	1.3(4)
N(4)#1-Mn-N(3)-C(4)	-178.7(4)
N(3)#1-Mn-N(3)-C(4)	174(100)
N(1)-Mn-N(3)-C(4)	90.3(4)
N(1)#1-Mn-N(3)-C(4)	-89.7(4)
N(4)#1-Mn-N(4)-C(6)	-165(100)
N(3)-Mn-N(4)-C(6)	-2.1(4)
N(3)#1-Mn-N(4)-C(6)	177.9(4)
N(1)-Mn-N(4)-C(6)	-94.6(4)
N(1)#1-Mn-N(4)-C(6)	85.4(4)
N(4)#1-Mn-N(4)-C(9)	14(100)
N(3)-Mn-N(4)-C(9)	176.5(4)
N(3)#1-Mn-N(4)-C(9)	-3.5(4)
N(1)-Mn-N(4)-C(9)	84.0(4)
N(1)#1-Mn-N(4)-C(9)	-96.0(4)
Mn-N(1)-C(1)-C(2)	76(8)
N(1)-C(1)-C(2)-C(2)#2	-14(8)
N(1)-C(1)-C(2)-C(3)	166(8)
C(2)#2-C(2)-C(3)-N(2)	13(18)
C(1)-C(2)-C(3)-N(2)	-167(17)
C(11)#1-N(3)-C(4)-C(5)	-176.8(4)
Mn-N(3)-C(4)-C(5)	1.9(7)
C(11)#1-N(3)-C(4)-C(13)#1	2.5(5)
Mn-N(3)-C(4)-C(13)#1	-178.9(3)

N(3)-C(4)-C(5)-C(6)	-5.3(8)
C(13)#1-C(4)-C(5)-C(6)	175.6(5)
N(3)-C(4)-C(5)-C(14)	173.3(4)
C(13)#1-C(4)-C(5)-C(14)	-5.8(7)
C(9)-N(4)-C(6)-C(5)	-179.1(4)
Mn-N(4)-C(6)-C(5)	-0.3(6)
C(9)-N(4)-C(6)-C(7)	-0.6(5)
Mn-N(4)-C(6)-C(7)	178.2(3)
C(4)-C(5)-C(6)-N(4)	4.4(7)
C(14)-C(5)-C(6)-N(4)	-174.2(4)
C(4)-C(5)-C(6)-C(7)	-173.8(5)
C(14)-C(5)-C(6)-C(7)	7.6(7)
N(4)-C(6)-C(7)-C(8)	-0.5(6)
C(5)-C(6)-C(7)-C(8)	178.0(4)
C(6)-C(7)-C(8)-C(9)	1.4(6)
C(6)-N(4)-C(9)-C(10)	-177.0(4)
Mn-N(4)-C(9)-C(10)	4.2(6)
C(6)-N(4)-C(9)-C(8)	1.5(5)
Mn-N(4)-C(9)-C(8)	-177.3(3)
C(7)-C(8)-C(9)-N(4)	-1.9(5)
C(7)-C(8)-C(9)-C(10)	176.6(5)
N(4)-C(9)-C(10)-C(11)	-0.5(7)
C(8)-C(9)-C(10)-C(11)	-178.8(4)
N(4)-C(9)-C(10)-C(20)	-178.7(4)
C(8)-C(9)-C(10)-C(20)	3.0(7)
C(9)-C(10)-C(11)-N(3)#1	-3.1(7)
C(20)-C(10)-C(11)-N(3)#1	175.1(4)
C(9)-C(10)-C(11)-C(12)	177.9(5)
C(20)-C(10)-C(11)-C(12)	-3.9(7)
N(3)#1-C(11)-C(12)-C(13)	-2.7(6)
C(10)-C(11)-C(12)-C(13)	176.4(5)
C(11)-C(12)-C(13)-C(4)#1	1.1(6)
C(6)-C(5)-C(14)-C(19)	-80.9(6)
C(4)-C(5)-C(14)-C(19)	100.4(6)
C(6)-C(5)-C(14)-C(15)	97.9(5)
C(4)-C(5)-C(14)-C(15)	-80.8(6)

C(19)-C(14)-C(15)-C(16)	-0.7(8)
C(5)-C(14)-C(15)-C(16)	-179.5(4)
C(14)-C(15)-C(16)-C(17)	-0.1(8)
C(15)-C(16)-C(17)-C(18)	0.5(8)
C(15)-C(16)-C(17)-I(1)	180.0(4)
C(16)-C(17)-C(18)-C(19)	-0.1(8)
I(1)-C(17)-C(18)-C(19)	-179.6(4)
C(15)-C(14)-C(19)-C(18)	1.1(8)
C(5)-C(14)-C(19)-C(18)	179.9(5)
C(17)-C(18)-C(19)-C(14)	-0.7(9)
C(11)-C(10)-C(20)-C(21)	116.6(5)
C(9)-C(10)-C(20)-C(21)	-65.1(6)
C(11)-C(10)-C(20)-C(25)	-64.2(6)
C(9)-C(10)-C(20)-C(25)	114.1(5)
C(25)-C(20)-C(21)-C(22)	-0.7(7)
C(10)-C(20)-C(21)-C(22)	178.5(4)
C(20)-C(21)-C(22)-C(23)	1.1(8)
C(21)-C(22)-C(23)-C(24)	-1.3(8)
C(21)-C(22)-C(23)-I(2)	178.5(4)
C(22)-C(23)-C(24)-C(25)	1.1(8)
I(2)-C(23)-C(24)-C(25)	-178.7(4)
C(23)-C(24)-C(25)-C(20)	-0.7(8)
C(21)-C(20)-C(25)-C(24)	0.5(7)
C(10)-C(20)-C(25)-C(24)	-178.7(5)
C(26)-C(27)-C(28)-C(29)	179.6(9)
C(32)-C(27)-C(28)-C(29)	0.0
C(27)-C(28)-C(29)-C(30)	0.0
C(28)-C(29)-C(30)-C(31)	0.0
C(29)-C(30)-C(31)-C(32)	0.0
C(30)-C(31)-C(32)-C(27)	0.0
C(26)-C(27)-C(32)-C(31)	-179.7(8)
C(28)-C(27)-C(32)-C(31)	0.0

Symmetry transformations used to generate equivalent atoms:

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