Supporting Information

Synthesis, Crystal Growth, Optical and Magnetic Properties of Three Bimetallic Thiocyanates TBi(SCN)$_5$(T=Mn, Cd) and FeBi(SCN)$_6$

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Table S1. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

$MnBi(SCN)_5$						
Atom	**Wycoff**	***x***	***y***	***z***	**Occupation**	**U(eq)**
Bi1	2*i*	995.0(3)	1371.3(2)	7806.1(2)	1	29.74(7)
Mn1	2*i*	4309.9(10)	3756.2(8)	1733.9(8)	1	29.31(18)
S1	2*i*	5780(2)	7173.3(19)	3988.8(16)	1	51.1(4)
S2	2*i*	8266(3)	565.5(19)	3804(2)	1	60.6(5)
S3	2*i*	2626.5(19)	-193.2(16)	72.8(16)	1	38.1(3)
S4	2*i*	-336(2)	6402(3)	793(3)	1	88.3(8)
S5	2*i*	-901(2)	2693.6(19)	6264.4(16)	1	47.7(4)
N1	2*i*	5201(6)	5549(5)	2347(5)	1	38.7(11)
N2	2*i*	5896(6)	2182(6)	2665(5)	1	47.8(13)
N3	2*i*	3323(6)	2130(5)	1027(5)	1	38.8(11)
N4	2*i*	3138(6)	5612(5)	424(4)	1	31.7(10)
N5	2*i*	1897(6)	3298(5)	3627(5)	1	42.8(12)
C1	2*i*	5461(7)	6218(5)	2994(5)	1	32.6(12)
C2	2*i*	6866(8)	1525(6)	3120(6)	1	37.1(13)
C3	2*i*	3015(7)	1183(6)	646(5)	1	32.0(12)
C4	2*i*	1701(7)	5977(6)	609(5)	1	31.1(12)
C5	2*i*	767(7)	3050(6)	4701(6)	1	32.3(12)
$CdBi(SCN)_5$						
Atom	**Wycoff**	***x***	***y***	***z***	**Occupation**	**U(eq)**
Bi1	2*i*	9043.8(5)	8632.7(4)	2161.8(4)	1	36.19(14)

Cd1	2*i*	5743.2(9)	6280.8(8)	8202.5(7)	1	39.0(2)
S1	2*i*	7360(4)	10194(3)	9987(3)	1	46.9(7)
S2	2*i*	10998(4)	7348(4)	3607(3)	1	56.7(8)
S3	2*i*	4132(4)	2808(4)	6010(3)	1	60.9(9)
S4	2*i*	1661(5)	9449(4)	6231(4)	1	70.7(10)
S5	2*i*	10350(4)	3565(5)	9243(5)	1	100.2(16)
N1	2*i*	6892(11)	4341(9)	9572(8)	1	36(2)
N2	2*i*	8285(12)	6717(9)	6236(9)	1	48(2)
N3	2*i*	4775(12)	4416(10)	7603(10)	1	54(3)
N4	2*i*	6731(12)	7914(10)	8974(10)	1	56(3)
N5	2*i*	4086(13)	7896(10)	7291(10)	1	60(3)
C1	2*i*	7000(12)	8823(10)	9400(10)	1	35(2)
C2	2*i*	4496(13)	3746(11)	6970(10)	1	43(3)
C3	2*i*	3095(15)	8512(12)	6880(11)	1	44(3)
C4	2*i*	9379(15)	6994(11)	5166(12)	1	43(3)
C5	2*i*	8320(15)	4015(11)	9396(10)	1	41(3)

Table S2. Selected interatomic distances (Å) and bond angles (°) for $MnBi(SCN)_5$ and $CdBi(SCN)_5$.

$MnBi(SCN)_5$						
Atom Pair		Distance (Å)	Atom Set			Angle **(°)**
Bi1	$S1^3$	2.7049(15)	$S3^1$	Bi1	$S3^2$	89.06(4)
	$S2^4$	2.7572(15)	S5	Bi1	$S3^1$	81.92(4)
	$S3^1$	3.1492(15)	S5	Bi1	$S3^2$	170.07(4)
	$S3^2$	2.9611(15)	S5	Bi1	$S1^3$	97.33(5)
	$S4^5$	2.8303(15)	S5	Bi1	$S2^4$	84.05(5)

	S5	2.6676(15)	S5	Bi1	S4^{5}	92.26(5)
Mn1	N1	2.191(4)	S1^{3}	Bi1	S3^{2}	90.94(5)
	N2	2.169(5)	S1^{3}	Bi1	S3^{1}	171.14(4)
	N3	2.168(4)	S1^{2}	Bi1	S2^{4}	85.45(5)
	N4	2.294(4)	S1^{3}	Bi1	S4^{5}	90.76(5)
	N4^{6}	2.396(4)	S2^{4}	Bi1	S3^{1}	103.21(5)
	N5	2.179(5)	S2^{4}	Bi1	S3^{2}	102.14(4)
S1	C1	1.668(5)	S2^{4}	Bi1	S4^{5}	174.32(6)
S2	C2	1.659(6)	S4^{5}	Bi1	S3^{1}	80.46(5)
S3	C3	1.658(5)	S4^{5}	Bi1	S3^{2}	82.12(5)
S4	C4	1.626(5)	N4	Mn1	N4^{6}	81.94(15)
S5	C5	1.670(6)	N3	Mn1	N4^{6}	88.47(15)
N1	C1	1.136(6)	N3	Mn1	N4	88.29(16)
N2	C2	1.137(6)	N3	Mn1	N5	91.45(17)
N3	C3	1.143(6)	N3	Mn1	N1	175.07(17)
N4	C4	1.155(6)	N3	Mn1	N2	94.55(17)
N5	C5	1.142(6)	N5	Mn1	N4	94.20(17)
			N5	Mn1	N4^{6}	176.14(16)
			N5	Mn1	N1	88.71(16)
			N1	Mn1	N4	86.79(15)
			N1	Mn1	N4^{6}	91.05(15)
			N2	Mn1	N4	169.29(18)
			N2	Mn1	N4^{6}	87.81(17)
			N2	Mn1	N5	96.05(18)
			N2	Mn1	N1	90.33(17)
			N2	Mn1	N4	169.29(18)
			N2	Mn1	N4^{6}	87.81(17)
			N2	Mn1	N5	96.05(18)
			N2	Mn1	N1	90.33(17)
			C3	S3	Bi1^{1}	99.09(18)
			C5	S5	Bi1	97.03(18)
			C1	S1	Bi1^{3}	98.25(18)
			C2	S2	Bi1^{4}	95.06(18)

			C4	S4	Bi1^{5}	105.10(17)
			Mn1	N4	Mn1^{6}	98.06(15)
			C4	N4	Mn1	132.8(4)
			C4	N4	Mn1^{6}	127.9(4)
			C3	N3	Mn1	170.7(4)
			C5	N5	Mn1	171.8(5)
			C1	N1	Mn1	162.4(4)
			C2	N2	Mn1	170.8(5)
			N5	C5	S5	179.4(5)
			N3	C3	S3	178.5(5)
			N4	C4	S4	175.2(4)
			N1	C1	S1	178.1(5)
			N2	C2	S2	179.3(6)
			N4	C4	S4	175.2(4)

$CdBi(SCN)_5$

Atom Set		Distance (Å)	Atom Set			Angle **(°)**
Bi1	S1^{1}	3.164(4)	S1^{1}	Bi1	S1^{2}	89.10(10)
	S1^{2}	2.987(3)	S5	Bi	S1^{2}	169.78(11)
	S2^{4}	2.771(3)	S5	Bi1	S1^{1}	81.37(8)
	S3^{3}	2.713(3)	S5	Bi1	S3^{3}	97.40(10)
	S4^{5}	2.840(3)	S5	Bi1	S2^{4}	84.26(9)
	S5	2.675(3)	S5	Bi1	S4^{5}	92.45(11)
Cd1	N1	2.252(9)	S3^{3}	Bi1	S1^{2}	91.49(9)
Cd1	N2	2.263(10)	S3^{3}	Bi1	S1^{1}	171.38(8)
Cd1	N3	2.299(9)	S3^{3}	Bi1	S2^{3}	85.19(10)
Cd1	N4	2.411(8)	S3^{3}	Bi1	S4^{4}	90.79(10)
Cd1	N4^{6}	2.499(8)	S2^{4}	Bi1	S1^{1}	103.12(9)
Cd1	N5	2.304(10)	S2^{4}	Bi1	S1^{2}	101.58(10)
S1	C1	1.676(10)	S2^{4}	Bi1	S4^{4}	174.42(13)
S2	C2	1.684(11)	S4^{5}	Bi1	S1^{2}	82.35(9)
S3	C3	1.660(11)	S4^{5}	Bi1	S1^{1}	80.77(10)
S4	C4	1.652(12)	N5	Cd1	N4	94.6(3)
S5	C5	1.669(12)	N5	Cd1	N4^{6}	175.5(3)
N1	C1	1.148(11)	N4	Cd1	N4^{6}	80.9(3)
N2	C2	1.131(12)	N1	Cd1	N5	92.6(3)

N3	C3	1.144(11)	N1	Cd1	N4	88.0(3)
N4	C4	1.151(11)	N1	Cd1	N4^{6}	87.1(3)
N5	C5	1.137(12)	N1	Cd1	N3	173.9(3)
			N1	Cd1	N2	94.8(3)
			N3	Cd1	N5	89.5(3)
			N3	Cd1	N4	86.0(3)
			N3	Cd1	N4^{6}	90.3(3)
			N2	Cd1	N5	97.4(3)
			N2	Cd1	N4^{6}	87.1(3)
			N2	Cd1	N4	167.5(3)
			N2	Cd1	N3	90.6(3)
			C1	S1	Bi1^{1}	98.1(3)
			C5	S5	Bi1	96.9(4)
			C3	S3	Bi1^{3}	98.4(4)
			C2	S2	Bi1^{4}	94.6(3)
			C4	S4	Bi1^{5}	103.8(3)
			C5	N5	Cd1	170.1(9)
			Cd1	N4	Cd1^{6}	99.1(3)
			C4	N4	Cd1^{6}	127.5(8)
			C4	N4	Cd1	131.2(8)
			C1	N1	Cd1	170.1(9)
			C3	N3	Cd1	162.1(9)
			C2	N2	Cd1	169.4(9)
			N1	C1	S1	178.0(10)
			N5	C5	S5	178.3(10)
			N2	C2	S2	178.6(12)
			N4	C4	S4	176.2(9)
			N3	C3	S3	178.3(10)

^{1}1-X,2-Y,1-Z; ^{2}1+X,+Y,1+Z; ^{3}2-X,1-Y,1-Z; ^{4}2-X,2-Y,1-Z; ^{5}1-X,1-Y,1-Z; ^{6}1-X,1-Y,-Z

Table S3. Total energy values calculated for $MnBi(SCN)_5$ and $FeBi(SCN)_6$.

		$MnBi(SCN)_5$	$FeBi(SCN)_6$
DFT	FM	–236.57669 eV	–274.17084 eV
	AFM	–236.59681 eV	–274.84638 eV
DFT+U	FM	–236.91843eV	–270.85627 eV
	AFM	–236.92320 eV	–270.85645 eV

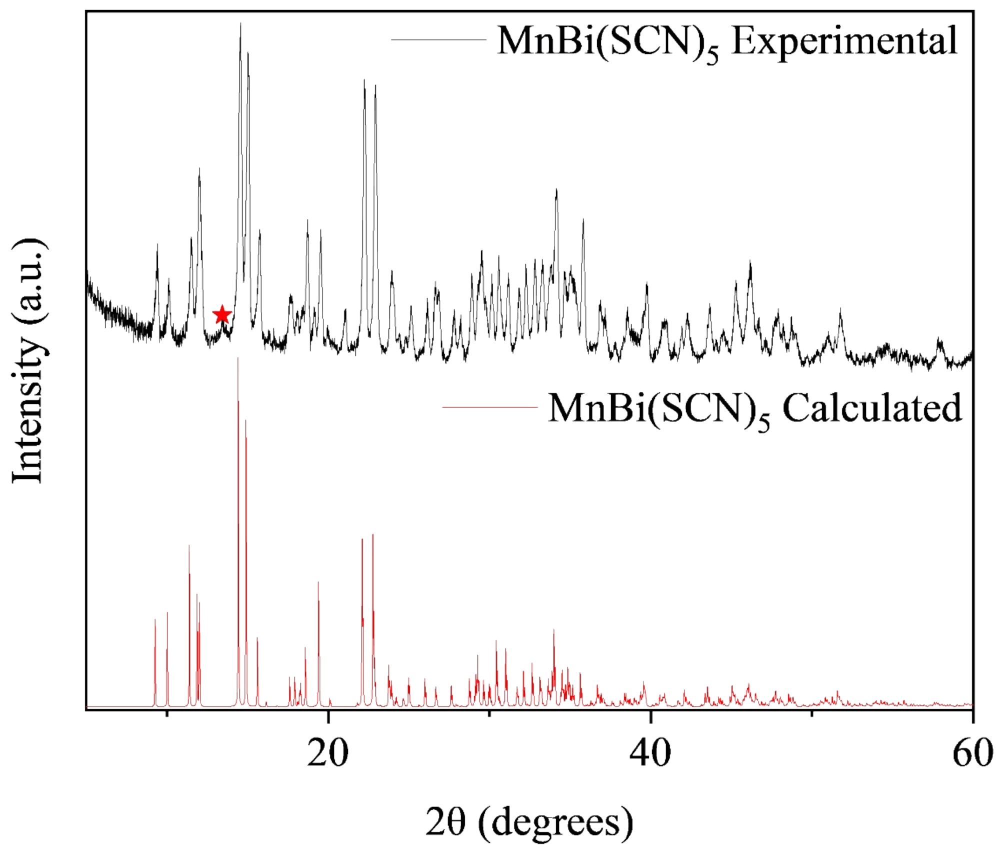

Figure S1. Lab experimental and simulated powder X-ray diffraction results for $MnBi(SCN)_5$, peaks corresponding to impurities indicated by star.

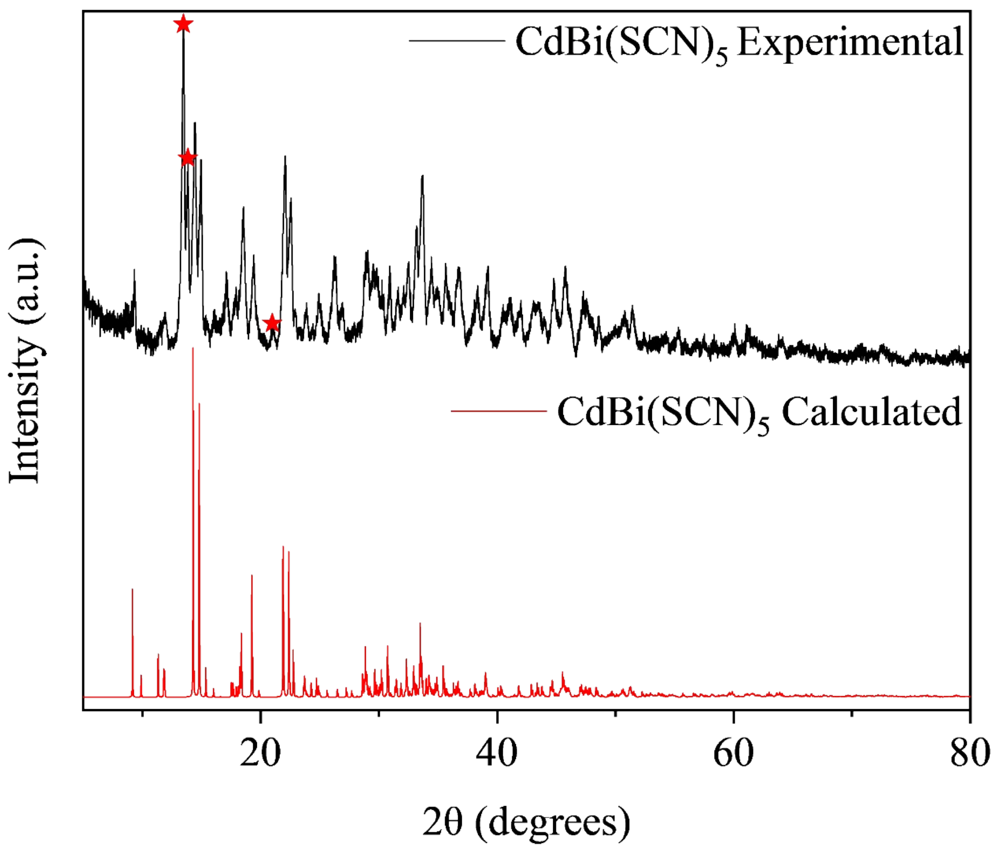

Figure S2. Lab experimental and simulated powder X-ray diffraction results for $CdBi(SCN)_5$, peaks corresponding to impurities indicated by star.

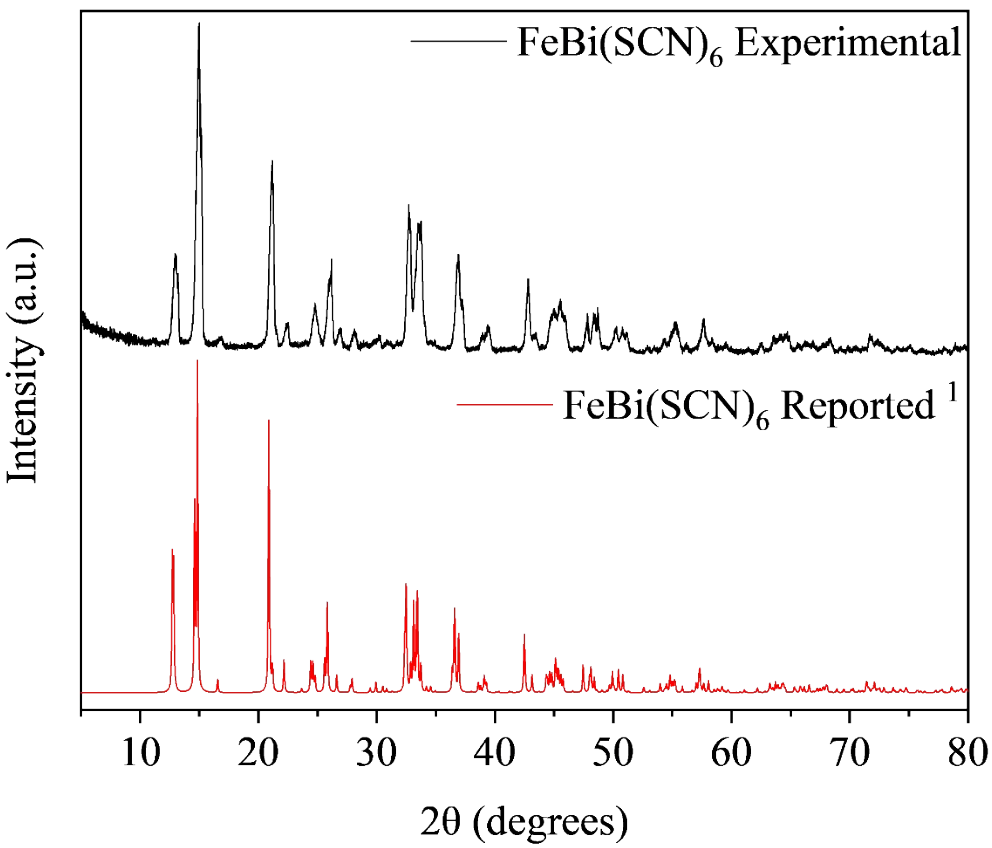

Figure S3. Lab experimental and reported powder [1] X-ray diffraction results for $FeBi(SCN)_6$

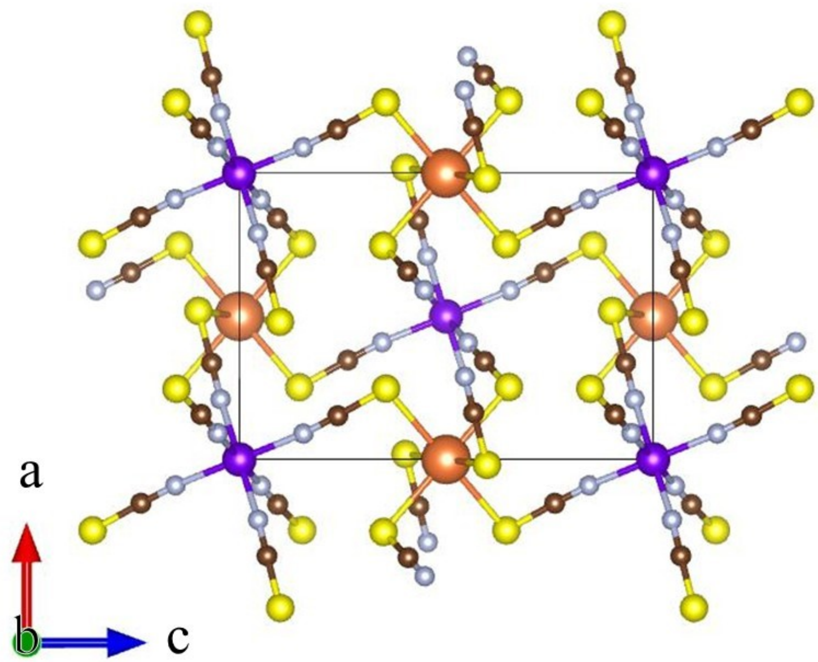

Figure S4. Structure of $FeBi(SCN)_6$ [1] viewed along [010]. Fe: purple, Bi: orange, S: yellow, C: brown, N: gray.

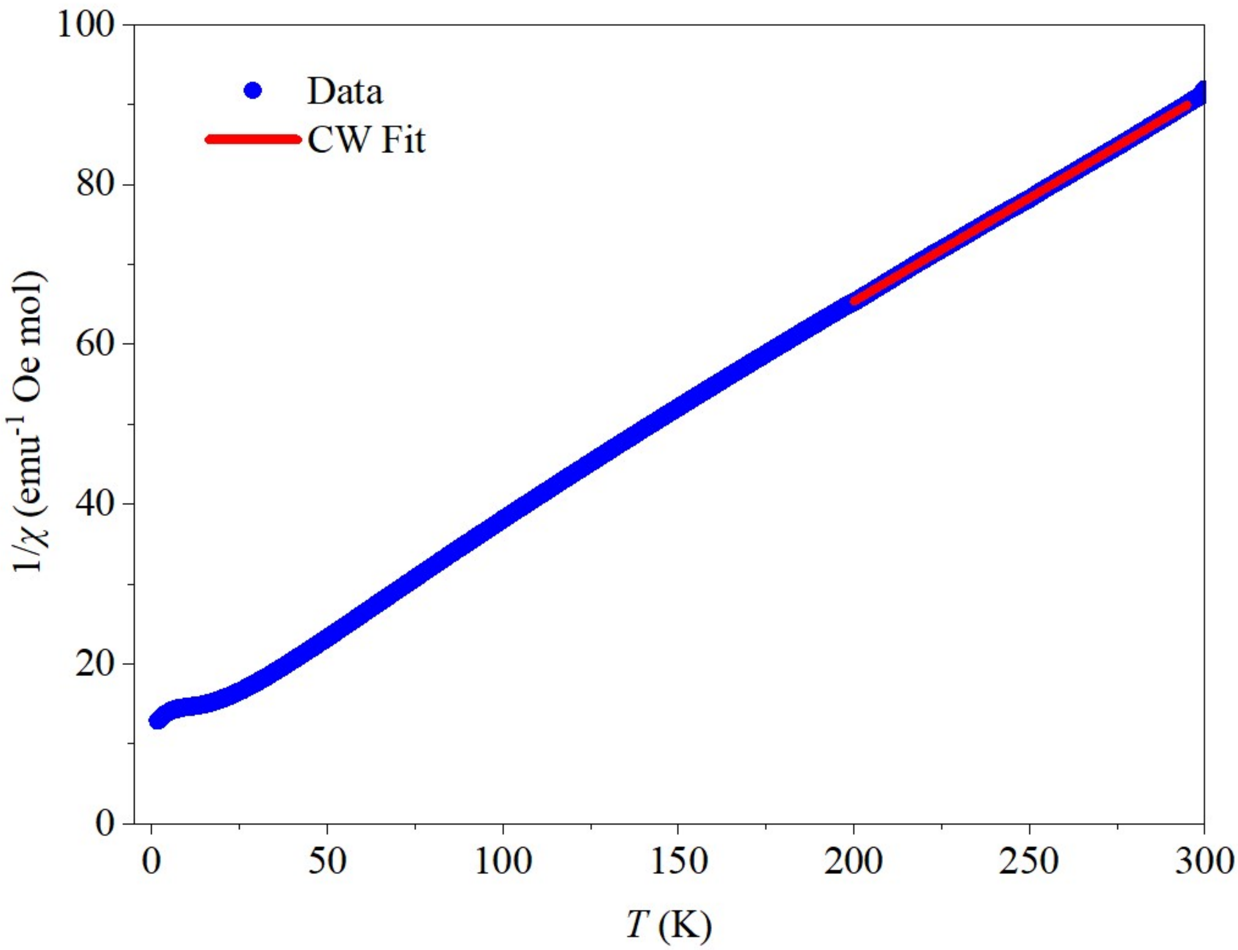

Figure S5. Fitting of magnetic susceptibility for $MnBi(SCN)_5$ to the Curie-Weiss formula $1/\chi = (T - \theta)/C$. The fitting yields a negative Weiss temperature $\theta = -52.52$ K and Curie constant $C = 3.86$ emu K mol^{-1} Oe^{-1}, which converts to an effective moment of 5.56 μ_B,

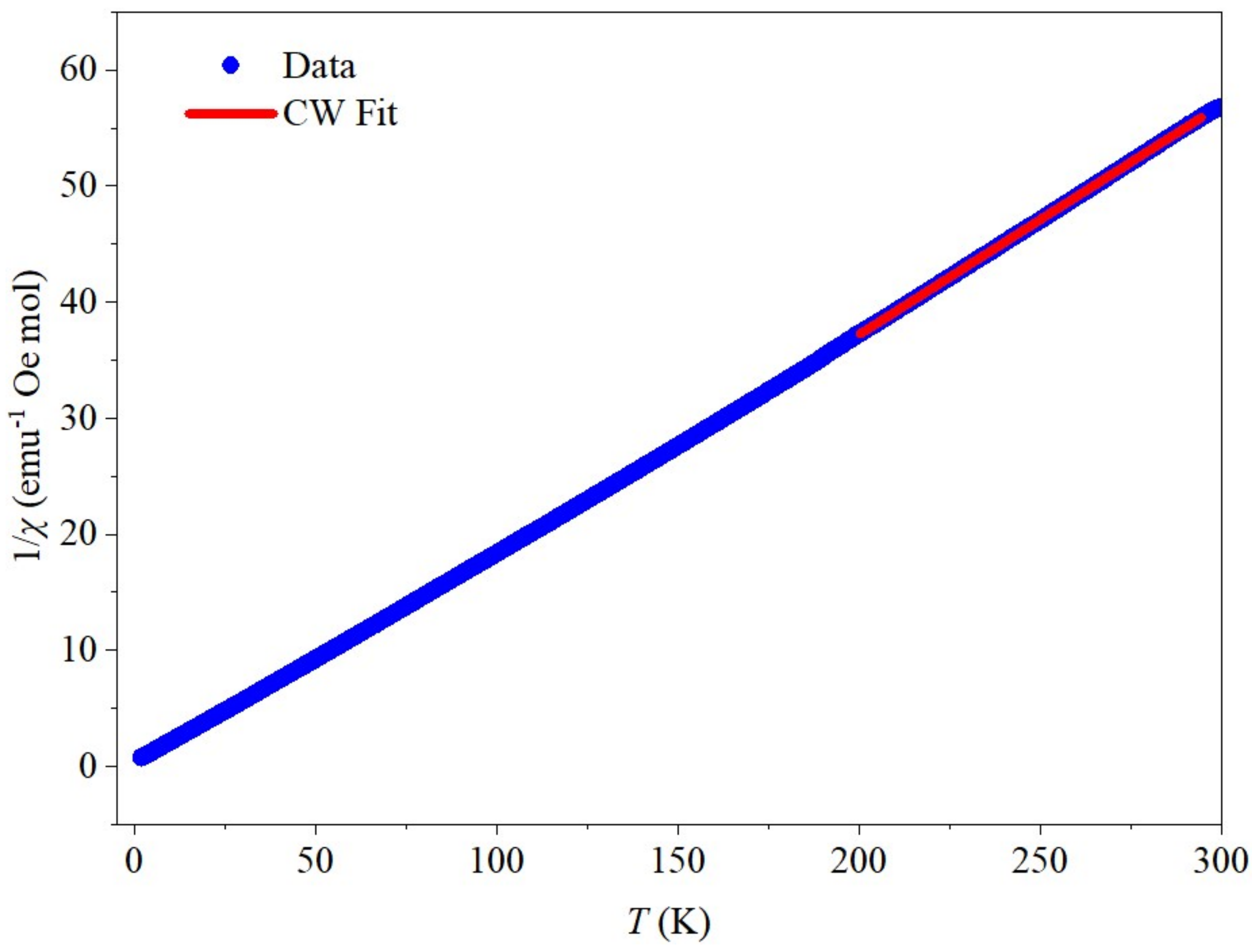

Figure S6. Fitting of magnetic susceptibility for $FeBi(SCN)_5$ to the Curie-Weiss formula $1/\chi = (T - \theta)/C$. The fitting yields a negative Weiss temperature $\theta = 12.01$ K and Curie constant $C = 5.05$ emu K mol^{-1} Oe^{-1}, which converts to an effective moment of 6.35 μ_B,

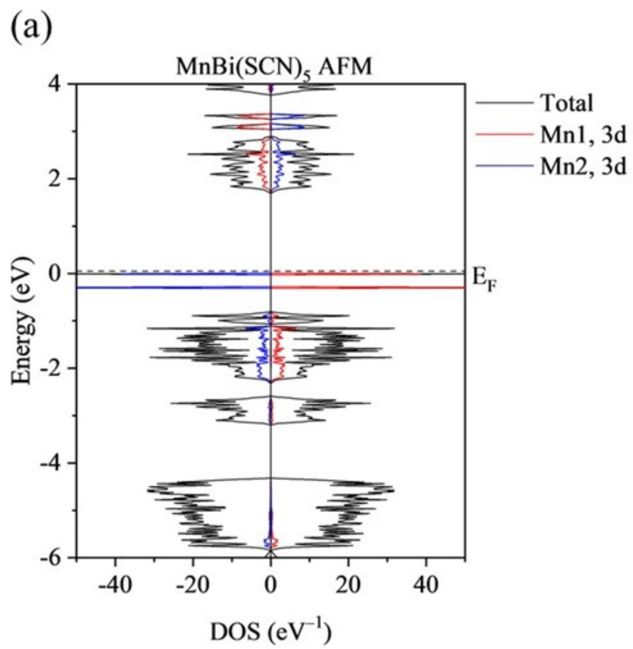

Figure S7. $MnBi(SCN)_5$ DOS calculated without Hubbard U parameter. (a) Total DOS and contributions of $(SCN)^-$ and Bi. (b) Total DOS and contribution of Mn 3d orbitals. AFM: antiferromagnetic model.

References

1 M. J. Cliffe, E. N. Keyzer, M. T. Dunstan, S. Ahmad, M. F. L. De Volder, F. Deschler, A. J. Morris and C. P. Grey, *Chem. Sci.*, 2019, **10**, 793–801.