Single-molecule magnet behavior in three cyano-bridged heterometallic Fe^{III}–Ni^{II} clusters

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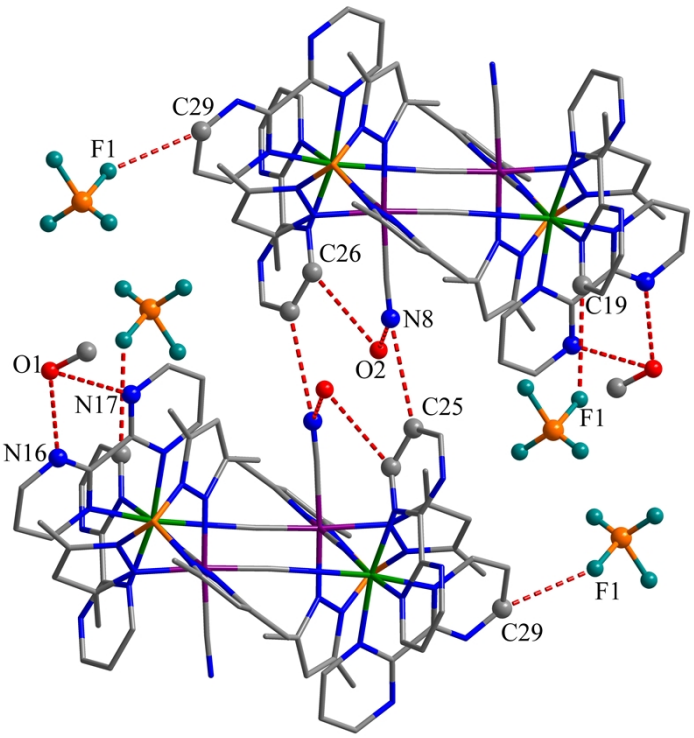

Figure S1. Packing diagram of **2**, the red dashed lines represent hydrogen bonding interactions. Hydrogen atoms are omitted for clarity (Fe, violet, Ni, green, C, gray, N, blue, B, orange, O, red, F, teal).

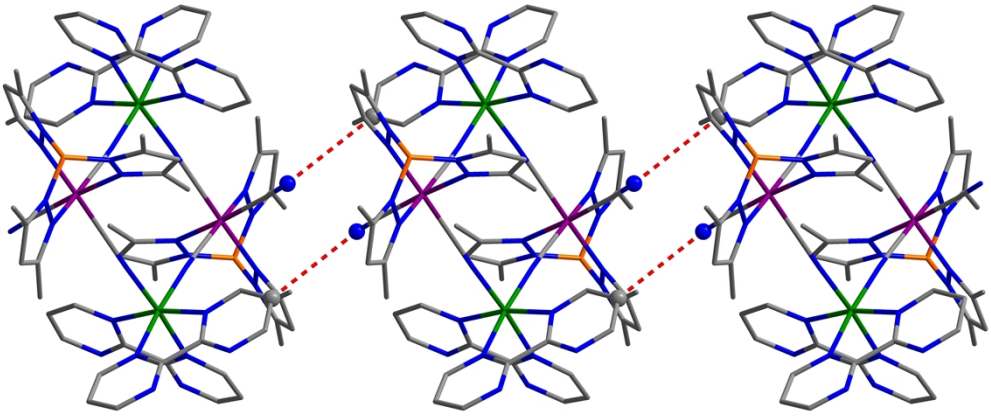

Figure S2. Crystal structure of 1D chain of **2**, the red dashed lines represent hydrogen bonding interactions. The anions, hydrogen atoms, methanol and water molecules are omitted for clarity (Fe, violet, Ni, green, C, gray, N, blue, B, orange).

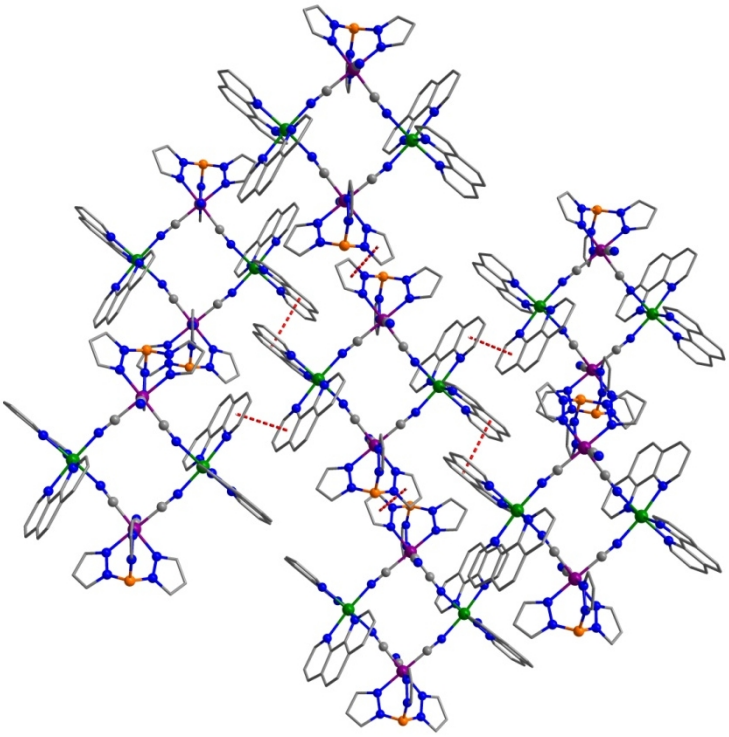

Figure S3. Packing diagram of **3**, the red dashed lines represent π–π stacking of pyrazolyl rings, benzen rings, and pyridine rings between adjacent chains. The anions are omitted for clarity (Fe, violet, Ni, green, C, gray, N, blue, B, orange).

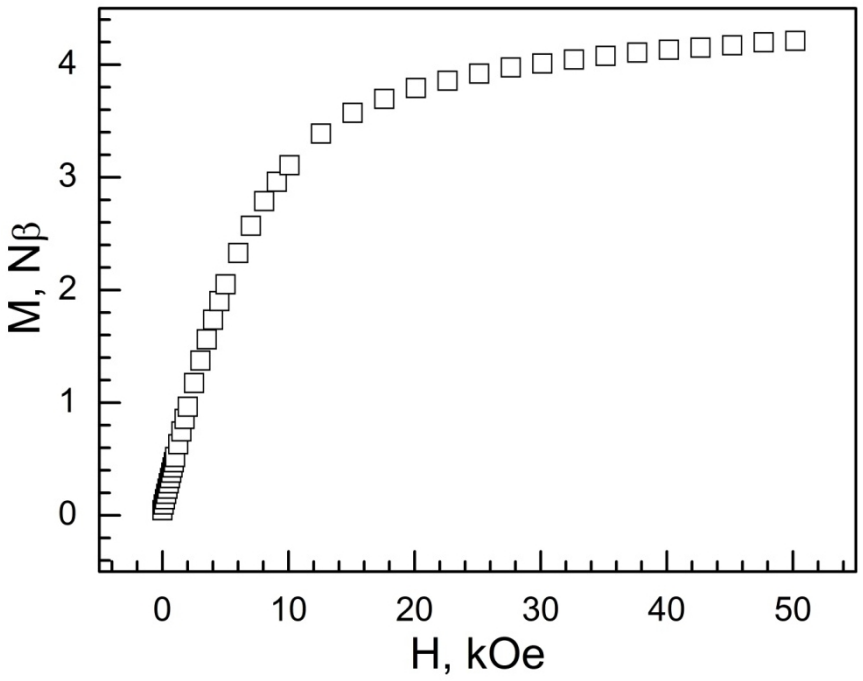

Figure S4. Field dependence of magnetization of **1** at 1.8 K.

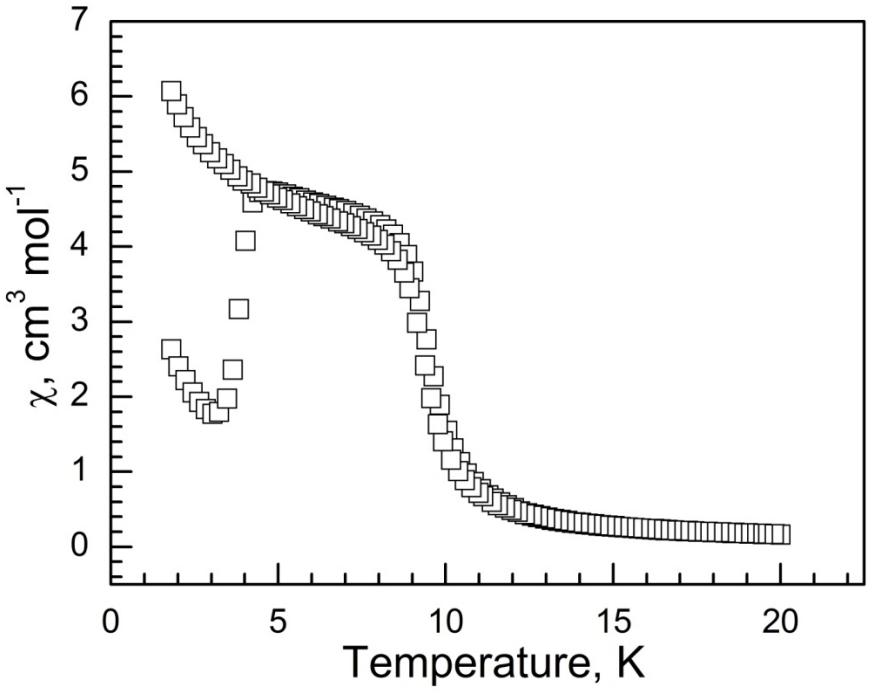

Figure S5. The irreversibility of ZFC and FC magnetization curves of **1** at 100 Oe.

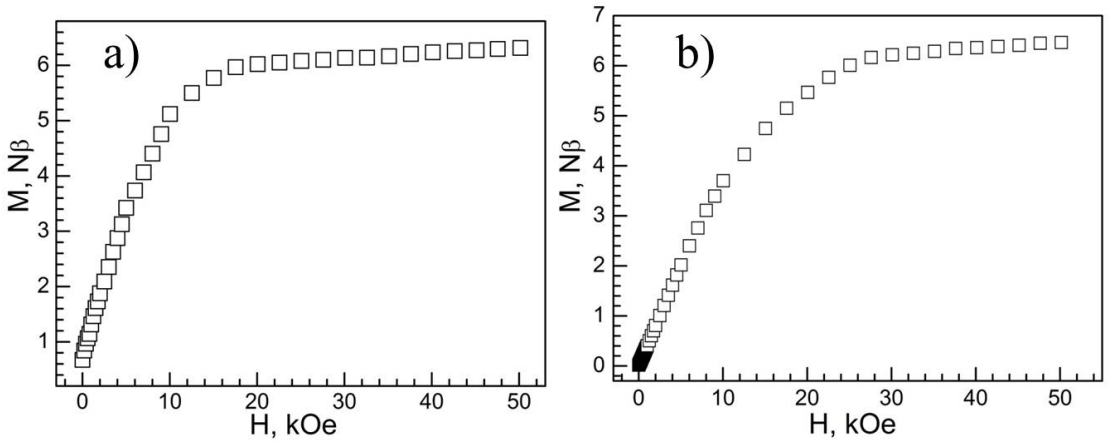

Figure S6. Field dependence of magnetization for **2** (a) and **3** (b) at 1.8 K.

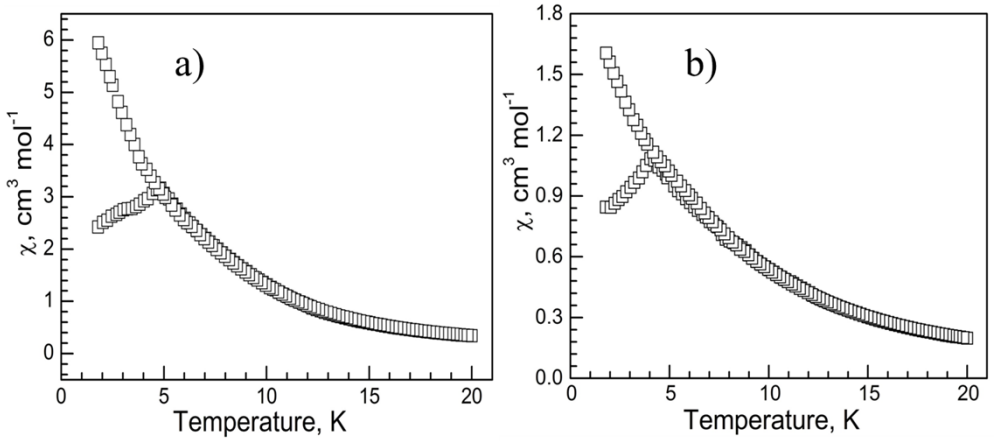

Figure S7. The irreversibility of ZFC and FC magnetization curves of **2** (a) and **3** (b) at 100 Oe.

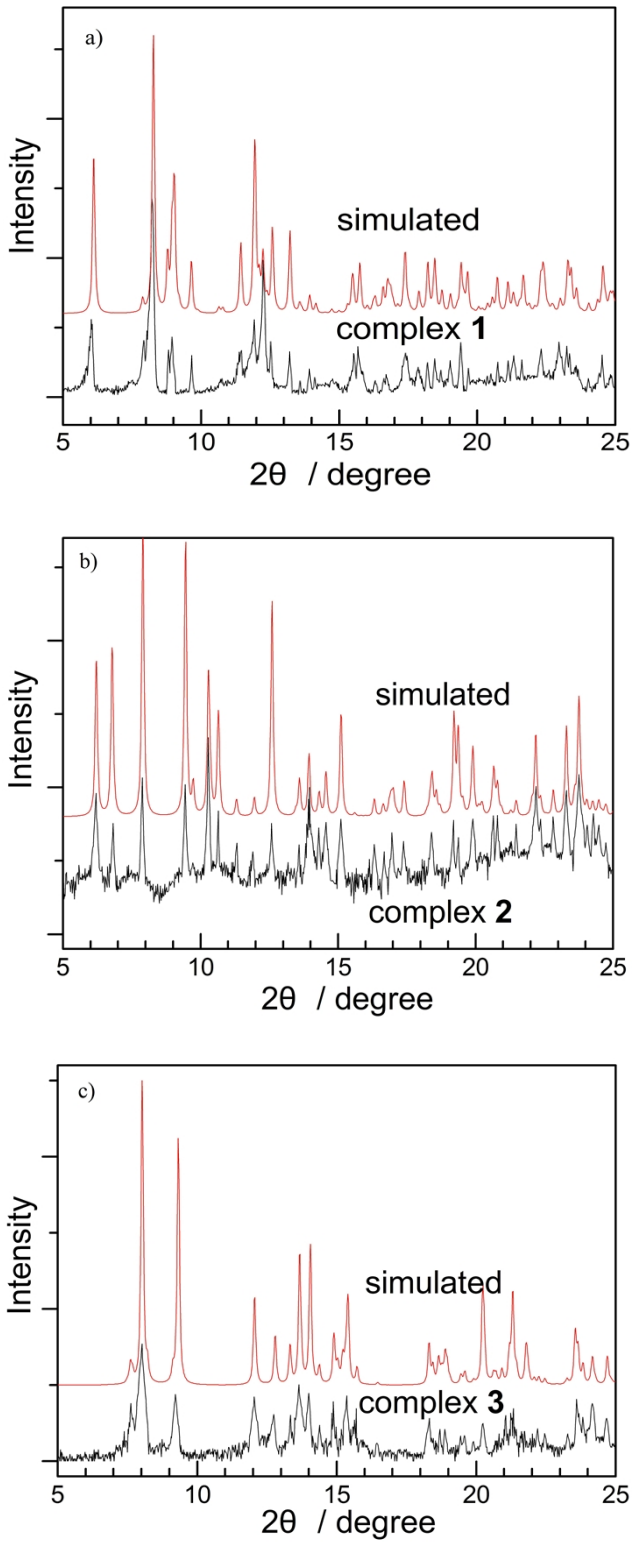

Figure S8. The experimental powder XRD pattern and the simulated XRD pattern of **1-3**.

Table S1 Selected bond lengths (Å) and angles (º) for **1**.

Complex **1**			
Fe(1)-C(15)	1.895(5)	Ni(1)-N(9)	2.074(3)
Fe(1)-C(14)	1.920(5)	Ni(1)-N(9)#1	2.074(3)
Fe(1)-C(13)	1.934(5)	Ni(1)-N(12)#1	2.112(4)
Fe(1)-N(6)	1.959(3)	Ni(1)-N(12)	2.112(4)
Fe(1)-N(7)	1.978(3)	Ni(1)-N(14)#1	2.117(4)
Fe(1)-N(4)	1.981(4)	Ni(1)-N(14)	2.117(4)
C(15)-Fe(1)-C(14)	89.2(2)	N(9)-Ni(1)-N(9)#1	180.00(17)
C(15)-Fe(1)-C(13)	86.5(2)	N(9)-Ni(1)-N(12)#1	89.94(14)
C(14)-Fe(1)-C(13)	84.64(18)	N(9)#1-Ni(1)-N(12)#1	90.06(14)
C(15)-Fe(1)-N(6)	91.69(19)	N(9)-Ni(1)-N(12)	90.06(14)
C(14)-Fe(1)-N(6)	177.08(17)	N(9)#1-Ni(1)-N(12)	89.94(14)
C(13)-Fe(1)-N(6)	92.65(16)	N(12)#1-Ni(1)-N(12)	180.000(1)
C(15)-Fe(1)-N(7)	90.34(18)	N(9)-Ni(1)-N(14)#1	90.39(15)
C(14)-Fe(1)-N(7)	92.74(17)	N(9)#1-Ni(1)-N(14)#1	89.60(15)
C(13)-Fe(1)-N(7)	175.89(17)	N(12)#1-Ni(1)-N(14)#1	90.23(15)
N(6)-Fe(1)-N(7)	90.02(14)	N(12)-Ni(1)-N(14)#1	89.77(15)
C(15)-Fe(1)-N(4)	177.43(18)	N(9)-Ni(1)-N(14)	89.61(15)
C(14)-Fe(1)-N(4)	91.7(2)	N(9)#1-Ni(1)-N(14)	90.39(15)
C(13)-Fe(1)-N(4)	96.02(16)	N(12)#1-Ni(1)-N(14)	89.77(15)
N(6)-Fe(1)-N(4)	87.49(15)	N(12)-Ni(1)-N(14)	90.23(15)
N(7)-Fe(1)-N(4)	87.22(15)	N(14)#1-Ni(1)-N(14)	180.000(1)

Symmetry transformations used to generate equivalent atoms for **1**: #1: -x, -y, -z+2.

Table S2 Selected bond lengths (Å) and angles (º) for **2**.

Complex **2**			
Fe(1)–C(18)	1.924(8)	Ni(1)-N(9)	2.040(7)
Fe(1)–C(17)	1.933(8)	Ni(1)-N(10)	2.074(6)
Fe(1)–C(16)	1.948(8)	Ni(1)-N(7)#1	2.074(6)
Fe(1)–N(5)	1.995(6)	Ni(1)-N(14)	2.076(6)
Fe(1)–N(1)	2.003(6)	Ni(1)-N(11)	2.084(6)
Fe(1)–N(3)	2.011(6)	Ni(1)-N(15)	2.114(6)
C(18)-Fe(1)-C(17)	83.8(3)	N(9)-Ni(1)-N(10)	92.8(2)
C(18)-Fe(1)-C(16)	85.4(3)	N(9)-Ni(1)-N(7)#1	93.2(2)
C(17)-Fe(1)-C(16)	88.6(3)	N(10)-Ni(1)-N(7)#1	97.0(2)
C(18)-Fe(1)-N(5)	93.4(3)	N(9)-Ni(1)-N(14)	95.3(3)
C(17)-Fe(1)-N(5)	177.0(3)	N(10)-Ni(1)-N(14)	169.5(2)
C(16)-Fe(1)-N(5)	92.4(3)	N(7)#1-Ni(1)-N(14)	89.1(2)
C(18)-Fe(1)-N(1)	95.1(3)	N(9)-Ni(1)-N(11)	89.1(2)
C(17)-Fe(1)-N(1)	91.3(3)	N(10)-Ni(1)-N(11)	78.6(2)
C(16)-Fe(1)-N(1)	179.5(3)	N(7)#1-Ni(1)-N(11)	175.2(2)
N(5)-Fe(1)-N(1)	87.7(2)	N(14)-Ni(1)-N(11)	94.8(2)
C(18)-Fe(1)-N(3)	173.9(3)	N(9)-Ni(1)-N(15)	173.6(2)
C(17)-Fe(1)-N(3)	91.7(3)	N(10)-Ni(1)-N(15)	93.6(2)
C(16)-Fe(1)-N(3)	90.3(3)	N(7)#1-Ni(1)-N(15)	86.3(2)
N(5)-Fe(1)-N(3)	91.2(2)	N(14)-Ni(1)-N(15)	78.3(3)
N(1)-Fe(1)-N(3)	89.2(2)	N(11)-Ni(1)-N(15)	92.0(2)

Symmetry transformations used to generate equivalent atoms for **2**: #1: -x+2, -y+2, -z+1.

Table S3 Selected bond lengths (Å) and angles (º) for **3**

Complex **3**			
Fe(1)-C(12)	1.910(5)	Ni(1)-N(9)	2.041(4)
Fe(1)-C(11)	1.913(4)	Ni(1)-N(8)#1	2.051(3)
Fe(1)-C(10)	1.928(6)	Ni(1)-N(13)	2.079(4)
Fe(1)-N(3)	1.961(3)	Ni(1)-N(10)	2.091(5)
Fe(1)-N(1)	1.975(4)	Ni(1)-N(12)	2.100(3)
Fe(1)-N(5)	1.972(4)	Ni(1)-N(11)	2.110(4)
C(12)-Fe(1)-C(11)	88.60(17)	N(9)-Ni(1)-N(8)#1	91.02(14)
C(12)-Fe(1)-C(10)	87.7(2)	N(9)-Ni(1)-N(13)	92.72(15)
C(11)-Fe(1)-C(10)	85.73(19)	N(8)#1-Ni(1)-N(13)	94.96(15)
C(12)-Fe(1)-N(3)	90.52(15)	N(9)-Ni(1)-N(10)	93.80(16)
C(11)-Fe(1)-N(3)	177.65(17)	N(8)#1-Ni(1)-N(10)	88.94(15)
C(10)-Fe(1)-N(3)	92.06(17)	N(13)-Ni(1)-N(10)	172.34(15)
C(12)-Fe(1)-N(1)	178.75(17)	N(9)-Ni(1)-N(12)	90.91(13)
C(11)-Fe(1)-N(1)	92.09(16)	N(8)#1-Ni(1)-N(12)	173.81(15)
C(10)-Fe(1)-N(1)	93.36(18)	N(13)-Ni(1)-N(12)	79.07(14)
N(3)-Fe(1)-N(1)	88.83(14)	N(10)-Ni(1)-N(12)	96.80(14)
C(12)-Fe(1)-N(5)	91.46(16)	N(9)-Ni(1)-N(11)	172.49(15)
C(11)-Fe(1)-N(5)	92.32(17)	N(8)#1-Ni(1)-N(11)	84.99(14)
C(10)-Fe(1)-N(5)	177.90(16)	N(13)-Ni(1)-N(11)	93.96(15)
N(3)-Fe(1)-N(5)	89.88(14)	N(10)-Ni(1)-N(11)	79.79(16)
N(1)-Fe(1)-N(5)	87.47(15)	N(12)-Ni(1)-N(11)	93.71(13)

Symmetry transformations used to generate equivalent atoms for **3**: #1: -x+2, -y+1, -z+1.

Table S4 Crystal data and structure refinement for complexes **1-3**

Complex	**1**	**2**	**3**
chemical formula	$C_{59}H_{76}B_2NiFe_2N_{30}O$	$C_{70}H_{80}B_4F_8Fe_2N_{34}Ni_2O_4$	$C_{72}H_{56}B_2Cl_2Fe_2N_{26}Ni_2O_{10}$
formula weight	1413.44	1885.92	1766.99
crystal system	Triclinic	Triclinic	Triclinic
space group	*P*−1	*P*−1	*P*−1
a /Å	11.9157(5)	11.365(3)	13.4477(8)
b /Å	16.0385(5)	13.635(3)	13.8536 (8)
c /Å	21.0439(7)	14.687(3)	13.9678(11)
α /deg	107.848(2)	104.044(16)	118.140(4)
β/ deg	96.552(2)	91.199(14)	114.968(4)
γ /deg	105.634(2)	99.696(15)	91.022(4)
V /Å^3	3600.6(2)	2171.8(9)	2002.1(2)
T/ K	296(2)	296(2)	296(2)
ρ/g cm^{-3}	1.290	1.413	1.464
μ (Mo K*α*)/mm^{-1}	0.717	0.838	0.958
θ range	$1.82° \le \theta \le 25.00°$	$1.82° \le \theta \le 25.00°$	$1.73° \le \theta \le 25.00°$
limiting indices	$-14 \le h \le 10$, $-18 \le k \le 19$, $-25 \le l \le 25$	$-13 \le h \le 12$, $-16 \le k \le 16$, $-17 \le l \le 14$	$-15 \le h \le 15$, $-16 \le k \le 15$, $-13 \le l \le 16$
reflns collected	24942	14637	11802
unique collected	12673	7630	7033
*R*int	0.0356	0.0525	0.0326
Goodness-of-fit on F^2	1.059	1.083	0.936
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0624, 0.1921	0.0918, 0.2473	0.0538, 0.1471
*R*1, *wR*2 (*all data*)	0.0877, 0.2086	0.1144, 0.2574	0.0828, 0.1637