Four-coordinate Co(II) and Fe(II) complexes with bis(N-heterocyclic carbene)borate and their magnetic properties

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Electronic Supplementary Information

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed under a dry nitrogen atmosphere using the standard Schlenk techniques. Lithium diisopropylamide (LDA, 2.0 M in THF) and anhydrous $CoCl_2$ and $FeCl_2$ were purchased from Aldrich. Solvents (THF and hexane, CH_2Cl_2, $CHCl_3$) were dried and purified using conventional methods. The ligand $H_2Bc^{tBu}I$ was synthesized

according to the published procedure[1]. ^{1}H NMR spectra were collected in CD_2Cl_2 on a Bruker AM-500 spectrometer at room temperature. Elemental analyses were performed in a Perkin-Elmer 240C analytical instrument. Solid magnetic properties have been measured by a Quantum Design MPMS-XL SQUID magnetometer. Magnetic behavior in dichloromethane-*d* solution were investigated by Evans' method[2].

Preparation of square planar and tetrahedral [Co(Bc^{tBu})$_2$] ($\mathbf{1_{SP}}$, $\mathbf{1_{Td}}$)

At –40 °C, LDA (1.0 mL, 2.0 M in THF, 2.0 mmol) was added to the ligand precursor $H_2Bc^{tBu}I$ (388 mg, 1.0 mmol) in 20 mL of THF. The mixture was stirred at –40 °C for 2 h, and then brought to room temperature. Anhydrous $CoCl_2$ (64.9 mg, 0.5 mmol) was added to the mixture and stirred for 5 h. The mixture was concentrated under vacuum. The residue was extracted into hexane. At room temperature, slow evaporation of hexane solution of the mixture for 4-5 days afforded the light green crystalline $\mathbf{1_{SP}}$ and blue crystalline $\mathbf{1_{Td}}$, which were isolated by manual separation. When a dichloromethane solution of $\mathbf{1_{SP}}$ or $\mathbf{1_{Td}}$ was allowed to evaporated slowly at room temperature, a mixture of $\mathbf{1_{SP}}$ and a new crystalline product (co-crystal complex $\mathbf{1_{Mix}}$) was obtained, which could be manually separated. The purities of $\mathbf{1_{SP}}$-$\mathbf{1_{Mix}}$ are checked by powder X-ray diffraction. Experimental XRD patterns of $\mathbf{1_{SP}}$, $\mathbf{1_{Td}}$ and $\mathbf{1_{Mix}}$ are in accordance with simulated XRD patterns calculated from the single crystal structural data (Figs. S1a-S1c). Elemental analysis (%) calcd. for $\mathbf{1_{SP}}$ ($C_{28}H_{48}CoN_8B_2$): C, 58.25; H, 8.38; N, 19.41; Found: C, 58.30; H, 8.29; N, 19.49. For $\mathbf{1_{Td}}$

($C_{28}H_{48}CoN_8B_2$): C, 58.25; H, 8.38; N, 19.41; Found: C, 58.23; H, 8.34; N, 19.56. For $\mathbf{1_{Mix}}$ ($C_{28}H_{48}CoN_8B_2$): C, 58.25; H, 8.38; N, 19.41; Found: C, 58.35; H, 8.21; N, 19.48.

Preparation of [Fe(Bc^{tBu})$_2$] (2).

At –40 °C, LDA (1.0 mL, 2.0 M in THF, 2.0 mmol) was added to the ligand precursor $H_2Bc^{tBu}I$ (388 mg, 1.0 mmol) in 20 mL of THF. The mixture was stirred at –40 °C for 2 h, and then brought to room temperature. Anhydrous $FeCl_2$ (63.4 mg, 0.5 mmol) was added to the mixture and stirred for 5 h. The mixture was concentrated under vacuum. The residue was extracted into hexane. **2** were crystallized by diffusing in diethyl ether/hexane under a dry nitrogen atmosphere. Experimental XRD patterns of **2** is in accordance with simulated XRD patterns calculated from the single crystal structure data (Fig. S1d). Elemental analysis (%) calcd. For $C_{28}H_{44}B_2FeN_8$: C, 58.57; H, 8.43; N, 19.51. Found C, 58.38; H, 8.51; N, 19.02.

X-ray Crystallography

Diffraction intensity of $\mathbf{1_{SP}}$, $\mathbf{1_{Td}}$, $\mathbf{1_{Mix}}$ or **2** were collected on a Bruker Smart CCD diffractometer equipped with graphite-monochromated Mo-Ka radiation. Direct methods were used to solve their structures Then the structures were refined with the full-matrix least squares technique using the program SHELXTL.[3] Among the three independent molecules of $\mathbf{1_{Td}}$, some atoms of the two molecules were found to have large thermal ellipsoids, which were modelled appropriately with 1358 restraints. In the molecule involving Co1, one B atom linking with N2c and N4c was modelled as disordering in two positions (B1c and B1d) with the same thermal ellipsoids. For the B atom (B1i) linking with N2i and N4i in the other molecule involving Co3, no suitable positions could be found, it was modeling with restraint of same thermal

ellipsoids. For the disordered tert-butyl groups, the following restraints were used: C-C bonds were restrainted to be 1.53(2) Å, the distance between methyl carbons in the same tert-butyl group were restrained to be equal, and the distance of carbon atom and nitrogen linking with tertiary butyl group were also restrained to be equal. All the disorder carbon atoms in tertiary butyl group were restrained to have same thermal ellipsoids. For $\mathbf{1_{Mix}}$, a tertiary carbon C25 and the methyl groups with large thermal ellipsoids are modeled as disordering in two positions. One boron atom (B6) was restrained.

Table S1. Crystallographic Data for $\mathbf{1_{SP}}$, $\mathbf{1_{Td}}$, $\mathbf{1_{Mix}}$ and **2**

	$\mathbf{1_{SP}}$	$\mathbf{1_{Td}}$	$\mathbf{1_{Mix}}$	**2**
Formula	$C_{28}H_{44}B_2CoN_8$	$C_{28}H_{44}B_2CoN_8$	$C_{28}H_{44}B_2CoN_8$	$C_{28}H_{44}B_2FeN_8$
CCDC no	1014795	1014796	1014797	1014798
Formula weight	577.29	577.29	577.29	574.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	Cc	P2(1)/c	Cc
a(Å)	10.9379(7)	30.413(2)	29.1539(10)	30.159(4)
b(Å)	13.6742(9)	17.3135(12)	17.0356(6)	17.138(2)
c(Å)	11.1977(8)	19.9580(14)	20.1403(7)	19.392(3)
α(°)	90	90	90	90
β(°)	114.1840(10)	113.390(10)	105.2400(10)	112.300(2)
γ(°)	90	90	90	90
V(Å^3)	1527.82(18)	9645.4(12)	9651.0(6)	9273(2)
D_{calc} (g/cm^3)	1.255	1.193	1.192	1.234
Z	2	12	12	4
T(K)	296(2)	296(2)	296(2)	173(2)
F (000)	618	3708	3708	3696
absorpt coefficient (mm^{-1})	0.593	0.564	0.564	0.519
θ range for data collection (°)	2.19 to 28.23	1.38 to 27.50	0.72 to 27.52	1.39 to 26.00
Data/restr/paras	3762 / 0 / 184	17848/1358/1435	22153/156 /1192	18012 / 2 / 1090

Reflections collected	10758	43484	65346	36121
Reflections unique	3762	17848	22153	18012
Completeness to θ(°)	28.23	27.50	27.52	26.00
R_{int}	0.0498	0.0725	0.0438	0.0369
Max./ min. transmission	0.908/ 0.863	0.880/ 0.843	0.920/0.872	0.908/0.886
Goodness-of-fit on F^2	1.057	1.016	1.012	1.005
R_1[a]/wR_2[b] [I >2σ(I)]	0.0463 / 0.0770	0.0582 / 0.1257	0.0602 / 0.1577	0.0339 / 0.0846
R_1/wR_2 (all data)	0.0821 / 0.0870	0.1030 / 0.1470	0.1117 / 0.1840	0.0377 / 0.0867
Larg peak and hole(e/Å^3)	0.352 / -0.286	0.248 / -0.373	0.836 / -0.688	0.405 / -0.371

[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected Interatomic Distances (Å) and Angles (°) for $\mathbf{1_{SP}}$, $\mathbf{1_{Td}}$, $\mathbf{1_{Mix}}$ and **2**

1_{SP}			
bond length (Å)		bond angle (°)	
C(1)-Co(1)	1.9712(2)	C(1)#1-Co(1)-C(1)	180.00(9)
C(4)-Co(1)	2.002(2)	C(1)#1-Co(1)-C(4)	85.54(8)
Co(1)-C(1)#1	1.9712(2)	C(1)-Co(1)-C(4)	94.46(8)
Co(1)-C(4)#1	2.002(2)	C(1)#1-Co(1)-C(4)#1	94.46(8)
B(1)-N(3)#1	1.545(3)	C(1)-Co(1)-C(4)#1	85.54(8)
B(1)-N(1)	1.552(3)	C(4)-Co(1)-C(4)#1	180.00(15)
1_{Td}			
bond length (Å)		bond angle (°)	
C(1A)-Co(1)	2.058(5)	C(1C)-Co(1)-C(1A)	113.5(2)

C(1C)-Co(1)	2.055(5)	C(1C)-Co(1)-C(8C)	100.4(2)
C(8A)-Co(1)	2.065(5)	C(1A)-Co(1)-C(8C)	101.7(4)
C(8C)-Co(1)	2.061(5)	C(1C)-Co(1)-C(8A)	108.5(2)
B(1A)-N(1A)	1.556(9)	C(1A)-Co(1)-C(8A)	100.6(2)
B(1A)-N(3A)	1.553(8)	C(8C)-Co(1)-C(8A)	118.8(2)
B(1C)-N(2C)	1.69(3)	N(3A)-B(1A)-N(1A)	112.9(5)
B(1C)-N(4C)	1.52(3)	N(4C)-B(1C)-N(2C)	109.0(17)
B(1D)-N(2C)	1.49(2)	N(2C)-B(1D)-N(4C)	112.6(12)
B(1D)-N(4C)	1.65(2)		
C(1E)-Co(2)	2.088(5)	C(8E)-Co(2)-C(8G)	121.1(2)
C(1G)-Co(2)	2.078(5)	C(8E)-Co(2)-C(1G)	114.4(2)
C(8E)-Co(2)	2.060(6)	C(8G)-Co(2)-C(1G)	100.6(2)
C(8G)-Co(2)	2.061(5)	C(8E)-Co(2)-C(1E)	100.4(2)
B(1E)-N(2E)	1.576(10)	C(8G)-Co(2)-C(1E)	114.1(2)
B(1E)-N(4E)	1.549(10)	C(1G)-Co(2)-C(1E)	105.8(2)
B(1G)-N(2G)	1.564(9)	N(4E)-B(1E)-N(2E)	112.3(5)
B(1G)-N(4G)	1.528(9)	N(4G)-B(1G)-N(2G)	113.9(5)
C(1I)-Co(3)	2.058(5)	C(1I)-Co(3)-C(8K)	117.87(19)
C(1K)-Co(3)	2.069(5)	C(1I)-Co(3)-C(8I)	99.9(2)
C(8I)-Co(3)	2.060(5)	C(8K)-Co(3)-C(8I)	112.9(2)
C(8K)-Co(3)	2.058(5)	C(1I)-Co(3)-C(1K)	118.24(19)
B(1I)-N(2I)	1.525(9)	C(8K)-Co(3)-C(1K)	100.40(19)

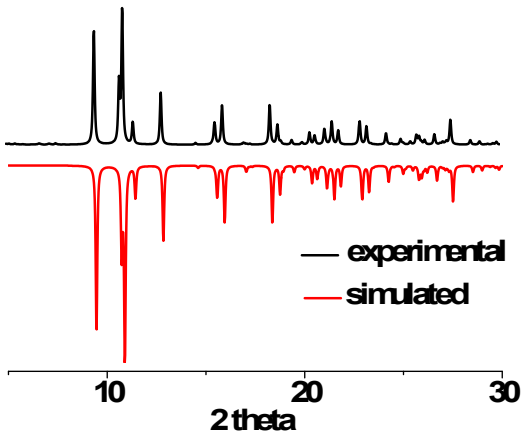
B(1I)-N(4I)	1.555(9)	C(8I)-Co(3)-C(1K)	115.5(5)
B(1K)-N(2K)	1.557(8)	N(2I)-B(1I)-N(4I)	111.0(10)
B(1K)-N(4K)	1.568(8)	N(2K)-B(1K)-N(4K)	112.2(5)

1_{Mix}

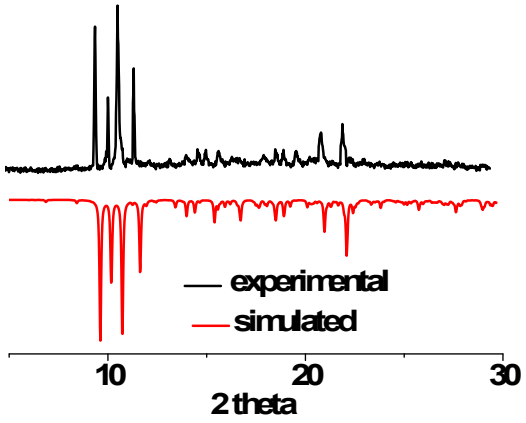
bond length (Å)		bond angle (°)	
C(1)-Co(1)	1.968(4)	C(1)-Co(1)-C(2)	84.14(14)
C(2)-Co(1)	1.974(3)	C(1)-Co(1)-C(3)	178.32(15)
C(3)-Co(1)	1.982(3)	C(2)-Co(1)-C(3)	97.50(14)
C(4)-Co(1)	1.987(4)	C(1)-Co(1)-C(4)	94.76(15)
B(1)-N(2)	1.540(5)	C(2)-Co(1)-C(4)	178.64(15)
B(1)-N(3)	1.558(5)	C(3)-Co(1)-C(4)	83.60(15)
B(2)-N(6)	1.548(6)	N(2)-B(1)-N(3)	105.(3)
B(2)-N(7)	1.548(6)	N(6)-B(2)-N(7)	106.2(3)
C(29)-Co(2)	2.063(3)	C(29)-Co(2)-C(32)	117.34(13)
C(30)-Co(2)	2.073(3)	C(29)-Co(2)-C(30)	99.84(13)
C(31)-Co(2)	2.083(4)	C(32)-Co(2)-C(30)	117.78(13)
C(32)-Co(2)	2.071(3)	C(29)-Co(2)-C(31)	114.52(14)
B(3)-N(10)	1.558(6)	C(32)-Co(2)-C(31)	99.73(14)
B(3)-N(11)	1.553(6)	C(30)-Co(2)-C(31)	108.04(14)
B(4)-N(14)	1.532(6)	N(11)-B(3)-N(10)	113.0(3)
B(4)-N(15)	1.541(6)	N(14)-B(4)-N(15)	116.0(4)
C(57)-Co(3)	2.063(4)	C(59)-Co(3)-C(57)	113.61(14)

C(58)-Co(3)	2.065(4)	C(59)-Co(3)-C(60)	100.27(16)
C(59)-Co(3)	2.053(4)	C(57)-Co(3)-C(60)	112.70(14)
C(60)-Co(3)	2.063(4)	C(59)-Co(3)-C(58)	118.87(15)
B(5)-N(18)	1.533(6)	C(57)-Co(3)-C(58)	100.73(15)
B(5)-N(19)	1.555(6)	C(60)-Co(3)-C(58)	111.20(15)
B(6)-N(22)	1.527(6)	N(18)-B(5)-N(19)	114.8(3)
B(6)-N(23)	1.525(6)	N(23)-B(6)-N(22)	117.8(3)
2			
bond length (Å)		bond angle (°)	
C(1)-Fe(1)	2.114(2)	C(3)-Fe(1)-C(1)	119.78(9)
C(2)-Fe(1)	2.117(2)	C(3)-Fe(1)-C(2)	118.60(8)
C(3)-Fe(1)	2.106(2)	C(1)-Fe(1)-C(2)	98.52(9)
C(4)-Fe(1)	2.120(2)	C(3)-Fe(1)-C(4)	98.65(9)
B(1)-N(2)	1.569(3)	C(1)-Fe(1)-C(4)	108.45(9)
B(1)-N(3)	1.563(3)	C(2)-Fe(1)-C(4)	108.8(2)
B(2)-N(6)	1.553(4)	N(3)-B(1)-N(2)	112.8(2)
B(2)-N(7)	1.558(3)	N(7)-B(2)-N(6)	114.5(2)
C(29)-Fe(2)	2.110(2)	C(31)-Fe(2)-C(30)	119.39(9)
C(30)-Fe(2)	2.104(2)	C(31)-Fe(2)-C(32)	100.27(9)
C(31)-Fe(2)	2.091(2)	C(30)-Fe(2)-C(32)	113.23(9)
C(32)-Fe(2)	2.107(2)	C(31)-Fe(2)-C(29)	117.42(9)
B(3)-N(10)	1.554(3)	C(30)-Fe(2)-C(29)	100.41(9)

B(3)-N(11)	1.551(3)	C(32)-Fe(2)-C(29)	105.92(8)
B(4)-N(14)	1.551(3)	N(11)-B(3)-N(10)	112.51(19)
B(4)-N(15)	1.570(4)	N(15)-B(4)-N(14)	113.9(2)
C(57)-Fe(3)	2.102(2)	C(57)-Fe(3)-C(59)	122.48(8)
C(58)-Fe(3)	2.128(2)	C(57)-Fe(3)-C(58)	99.58(9)
C(59)-Fe(3)	2.104(2)	C(59)-Fe(3)-C(58)	115.29(9)
C(60)-Fe(3)	2.129(2)	C(57)-Fe(3)-C(60)	113.19(9)
B(5)-N(18)	1.563(3)	C(59)-Fe(3)-C(60)	100.38(9)
B(5)-N(19)	1.565(4)	C(58)-Fe(3)-C(60)	105.26(9)
B(6)-N(22)	1.550(3)	N(19)-B(5)-N(18)	113.0(2)
B(6)-N(23)	1.571(3)	N(23)-B(6)-N(22)	112.21(19)



(a)



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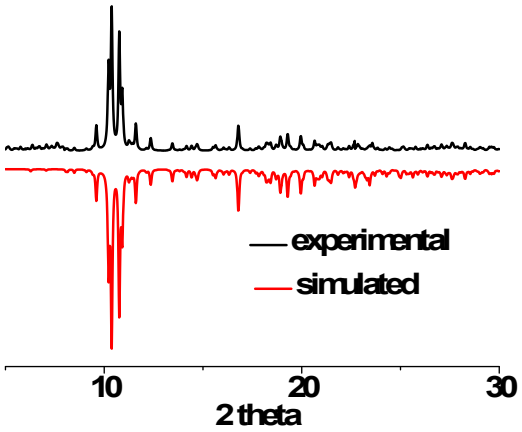

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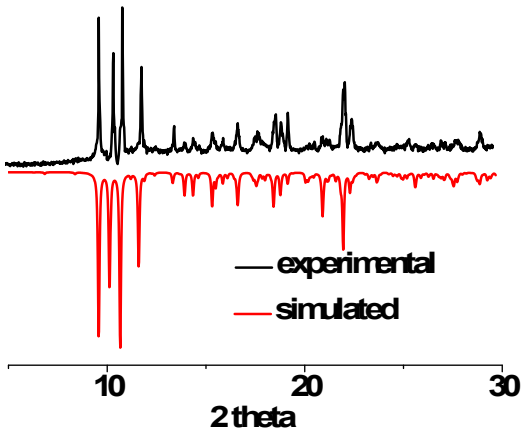

(d)

Fig.S1 Experimental and simulated XRD patterns of $\mathbf{1}_{SP}$ (a), $\mathbf{1}_{Td}$ (b), $\mathbf{1}_{Mix}$ (c) and **2** (d)

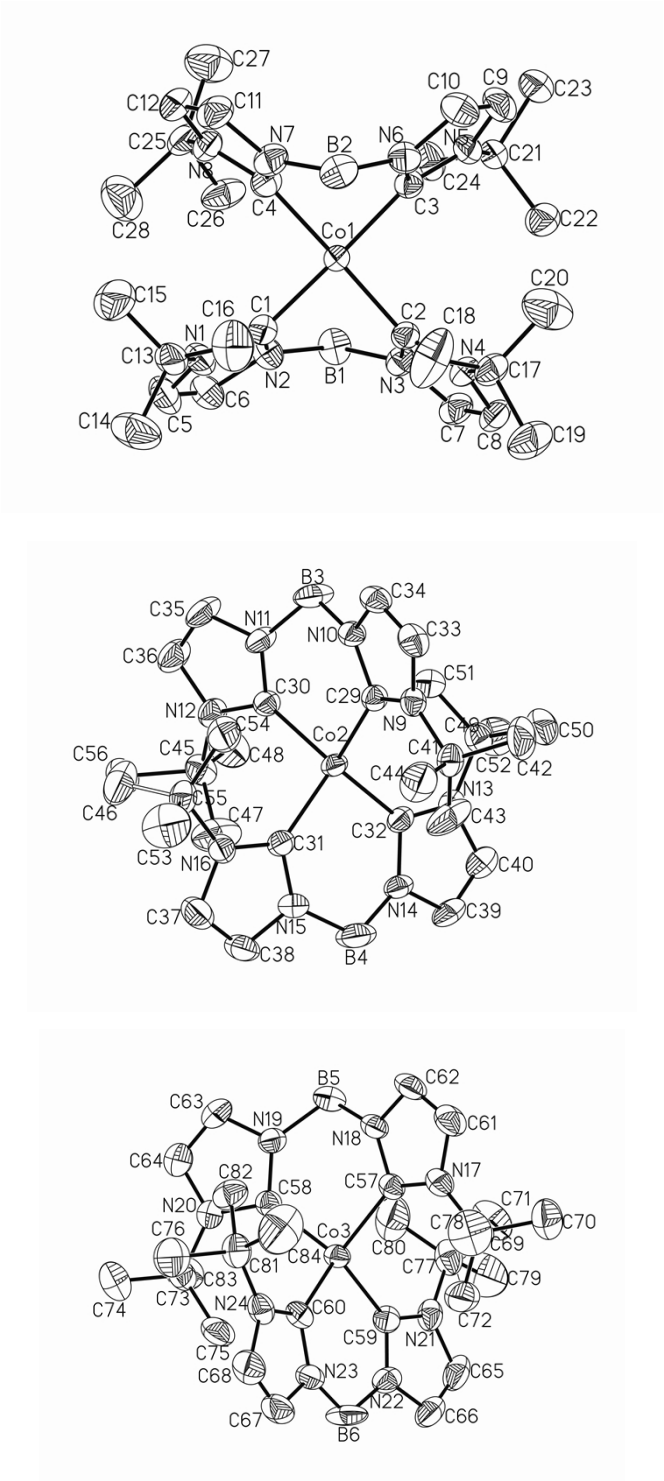

Fig. S2 Molecular structures of $\mathbf{1}_{\mathbf{Mix}}$ with 30% ellipsoids, hydrogen atoms are omitted for clarity.

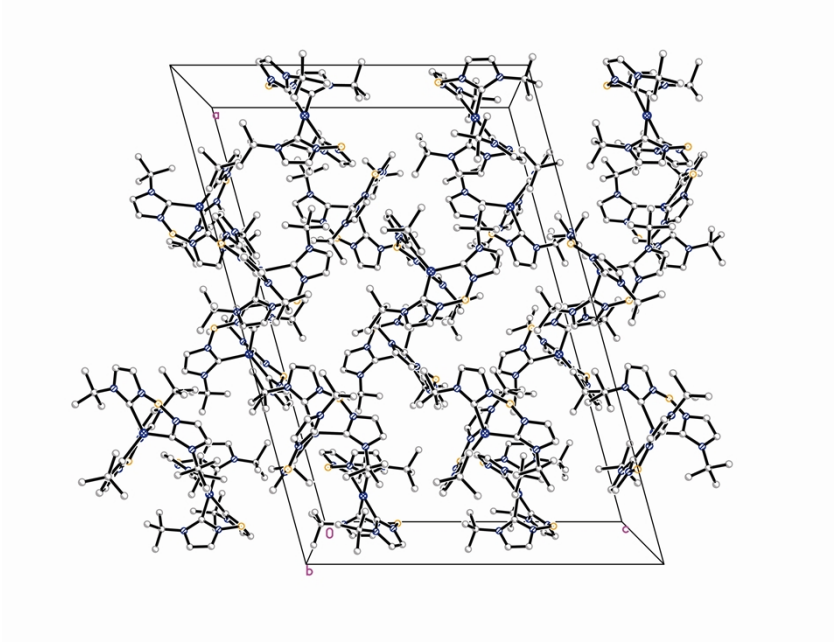

Fig. S3 The unit cell of $\mathbf{1}_{\mathbf{Mix}}$, hydrogen atoms are omitted for clarity

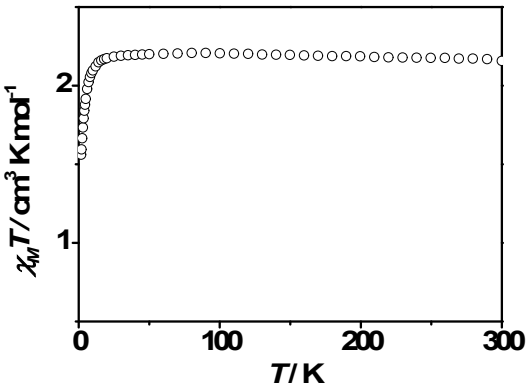

Fig. S4 Variable temperature dc magnetic susceptibility data for $\mathbf{1}_{\mathbf{Td}}$ under an applied dc field of 2000 Oe.

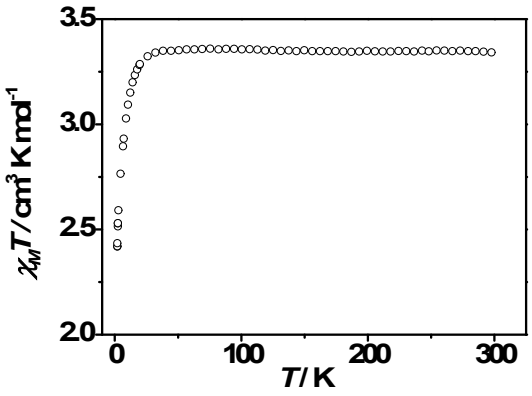

Fig. S5 Variable temperature dc magnetic susceptibility data for **2** under an applied dc field of 2000 Oe.

References

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