Electronic Supplementary Information

1,2-Diaza-4-phospholide Complexes of Chromium(II): A Dipotassium Organochromate Behaving as a Single-Molecule Magnet

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ESI-1. General Experimental Section

All manipulations were carried out in a nitrogen atmosphere under anaerobic conditions using standard Schlenk vacuum line and glove box techniques. The solvents were thoroughly dried, deoxygenated and distilled in a nitrogen atmosphere prior to use. The starting materials **3** and **4** were prepared according to the literatures. IR measurements were carried out on a Nicolet 360 FT-IR spectrometer from Nujol mulls prepared in a dry box. Melting points were measured in sealed nitrogen-filled capillaries without temperature correction with a XT4-100A apparatus (Electronic and Optical Instruments, Beijing, China). Elemental analysis was performed on an Elementarvario MACRO cube (Germany).

Preparation of {[(η^1-*N*-3,5-*t*Bu$_2$dp)$_4$Cr][(η^5(*N*,*N*,*C*,*C*,*P*)-K(η^2-(*O*,*O*-THF)$_2$)$_2$} (5). To a slurry of freshly prepared C_8K (0.33 g, 2.5mmol) in THF (10 mL) at 0°C was slowly added THF solution (15 mL) of **3** (0.46 g, 1.0 mmol) via a syringe. The solution was stirred overnight and then concentrated to about 10 mL. To this solution was added toluene (10 mL). The solution was filtered through Celite and the filtrate was concentrated to about 15 mL to give **5** as royal blue crystals at –30°C (0.17 g, 55%). M.p.: 260°C, decomp.. IR (KBr, Nujol mull, cm^{-1}): 1406(m), 1377(m), 1362(w), 1260(m), 1202(w), 1098(m), 1020(m), 907(w), 799(m), 682(m). Anal. calc. for $C_{63}H_{112}CrK_2N_8O_4P_4$(%): C 58.18; H 8.63; N 8.59. Found: C 57.92; H 8.81; N 8.36.

Preparation of {[(η^1-*N*-3,5-Ph$_2$dp)$_4$Cr](η^5(*N*,*N*,*C*,*C*,*P*)-K(η^2-(*O*,*O*-THF)$_2$)$_2$}$_\infty$ (6). To a slurry of freshly prepared C_8K (0.33 g, 2.5 mmol) in THF (10 mL) at 0°C was slowly added THF solution (15 mL) of **4** (0.50 g, 1.0 mmol) via a syringe. The solution was stirred overnight and turned red-brown from blue-green. The solution was concentrated to about 10 mL and the toluene (10 mL) was then added. The solution was filtered through Celite and the filtrate was concentrated to about 15 mL to give **6** as dark-red crystals at –30°C (0.16 g, 43%). M.p.: 220°C. IR (KBr, Nujol mull, cm^{-1}): 1599(m), 1496(m), 1444(m), 1379(m), 1251(m), 1057(ms), 1005(m), 915(m), 812(m), 767(s), 702(s), 625(m); Anal. Calc for $C_{72}H_{72}CrK_2N_8O_4P_4$(%): C 63.18; H 5.26; N 8.19. Found: C 63.44; H 5.12; N 8.36.

ESI-2. X-Ray Crystallography Data

The single-crystal X-ray diffraction data of compounds **5** and **6** were collected using a Agilent Xcalibur-G8930A CCD diffractometer operating at 50 kV and 20 mA using Mo Ka radiation (k = 0.71073 Å). Empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. The hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. Data collection and structural refinement parameters are given in Table ESI-1 and selected bond distances and angles are given in Table ESI-2. CCDC 1848497(**5**), 1848498(**6**) contain the crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table ESI-2-1. Crystal and Data Collection Parameters of Compounds **5** and **6**

Compound	**4**	**5**
Formula	$C_{63}H_{112}CrK_2N_8O_4P_4$	$C_{72}H_{72}CrK_2N_8O_4P_4$
Formula weight	1299.69	1367.46
Crystal size, mm	0.28 × 0.25 × 0.15	0.09 × 0.08 × 0.05
Crystal System	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	16.4723(9)	24.1285(18)
b, Å	24.2440(9)	16.1863(11)
c, Å	19.1309(6)	18.8547(10)
α, deg	90	90
β, deg	93.463(4)	101.428(6)
γ, deg	90	90
V, Å^3	7626.0(5)	7217.7(8)
Z	4	4
*D*c, gcm^{-3}	1.132	1.258

Absorption coefficient, mm^{-1}	0.388	0.415
F (000), e	2800	2856
T, K	293(2)	293(2)
Range, deg	2.97–26.34	3.05–25.35
Reflections measured	19185	20006
Unique reflections	7808	6602
$\theta_{\max}$, deg	26.34	25.35
R_{int}	0.0270	0.0788
Param. refined	396	411
Max and min transmission	1.0000 and 0.84945	1.0000and 0.25119
R_1, wR_2 [$I > 2\sigma(I)$]^{a}	0.0537, 0.1407	0.0776, 0.1955
R_1, wR_2 (all data)^{b}	0.0918, 0.1636	0.1513, 0.2488
Goodness-of-fit (GOF)	1.025	0.982
D (max), eÅ^{-3}	0.447	0.760
D (min), eÅ^{-3}	–0.498	–0.435

*^{a} $R_1 = \Sigma|Fo| - |Fc|/\Sigma|Fo|$. ^{b} $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{0.5}$.

Table ESI-2-2. Selected Bond Lengths [Å] and Angles [deg] for Compounds **5** and **6**

5				**6**			
Bonds	[Å]	Angles	[deg]	Bonds	[Å]	Angles	[deg]
Cr1–N4	2.122(2)	N4–Cr1–N4A	88.92(11)	Cr1–N3	2.069(4)	N3–Cr1–N3A	89.6(2)
Cr1–N4A	2.122(2)	N4–Cr1–N1A	172.30(8)	Cr1–N3A	2.069(4)	N3–Cr1–N1	90.57(15)
Cr1–N1A	2.128(2)	N4A–Cr1–N1A	91.61(8)	Cr1–N1	2.075(4)	N3A–Cr1–N1	172.28(15)
Cr1–N1	2.128(2)	N4–Cr1–N1	91.61(8)	Cr1–N1A	2.075(4)	N3–Cr1–N1A	172.28(15)
K1–N2	2.938(2)	N4A–Cr1–N1	172.30(8)	K1–N4	2.868(4)	N3A–Cr1–N1A	90.57(15)
K1–N2A	2.938(2)	N1A–Cr1–N1	88.89(11)	K1–N2	2.909(4)	N1–Cr1–N1A	90.3(2)
K1–centroid of dp ring	2.939(2)	O1–K1–O1A	73.70(18)	K1–centroid of dp ring	3.112(2)	O1A–K1–O2A	88.57(19)
		centroid–K1–centroid	103.24(5)			centroid–K1–centroid	99.05(6)

ESI-3. X-ray crystal structures of 5 and 6

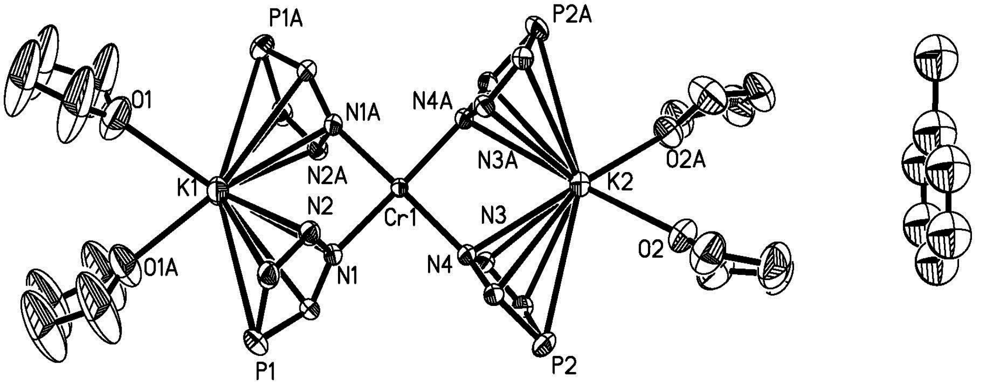

Figure ESI-3-1. X-ray crystal structures of **5**. Drawn with ellipsoids at 30%probability. H atoms and *t*Bu groups omitted for clarity. Selected bond distances [Å] and angles (deg): Cr1–N4 2.122(2), Cr1–N4A 2.122(2), Cr1–N1A 2.128(2), Cr1–N1 2.128(2), K1–N2 2.938(2), K1–N2A 2.938(2); N4–Cr1–N4A 88.92(11), N4–Cr1–N1A 172.30(8), N4A–Cr1–N1A 91.61(8), N4–Cr1–N1 91.61(8), N4A–Cr1–N1 172.30(8), N1A–Cr1–N1 88.89(11).

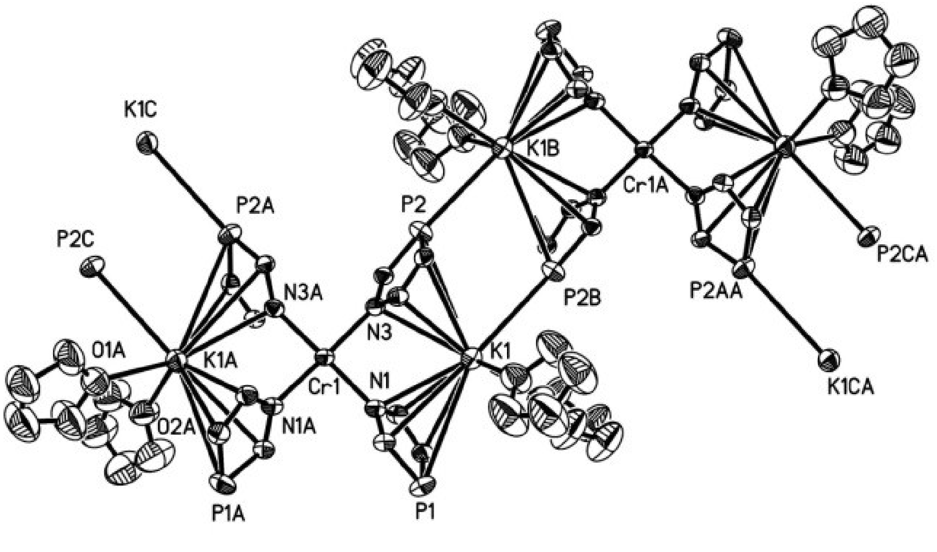

Figure ESI-3-2. X-ray crystal structure of **6**. Drawn with ellipsoids at 30% probability, toluene, Phenyl groups and hydrogen atoms omitted for clarity. Selected bond distances [Å], angles (deg): Cr1–N3 2.069(4), Cr1–N3A 2.069(4), Cr1–N1 2.075(4), Cr1–N1A 2.075(4), K1–N4 2.868(4), K1–N2 2.909(4); N3–Cr1–N3A 89.6(2), N3–Cr1–N1 90.57(15), N3A–Cr1–N1 172.28(15), N3–Cr1–N1A 172.28(15), N3A–Cr1–N1A 90.57(15), N1–Cr1–N1A 90.3(2).

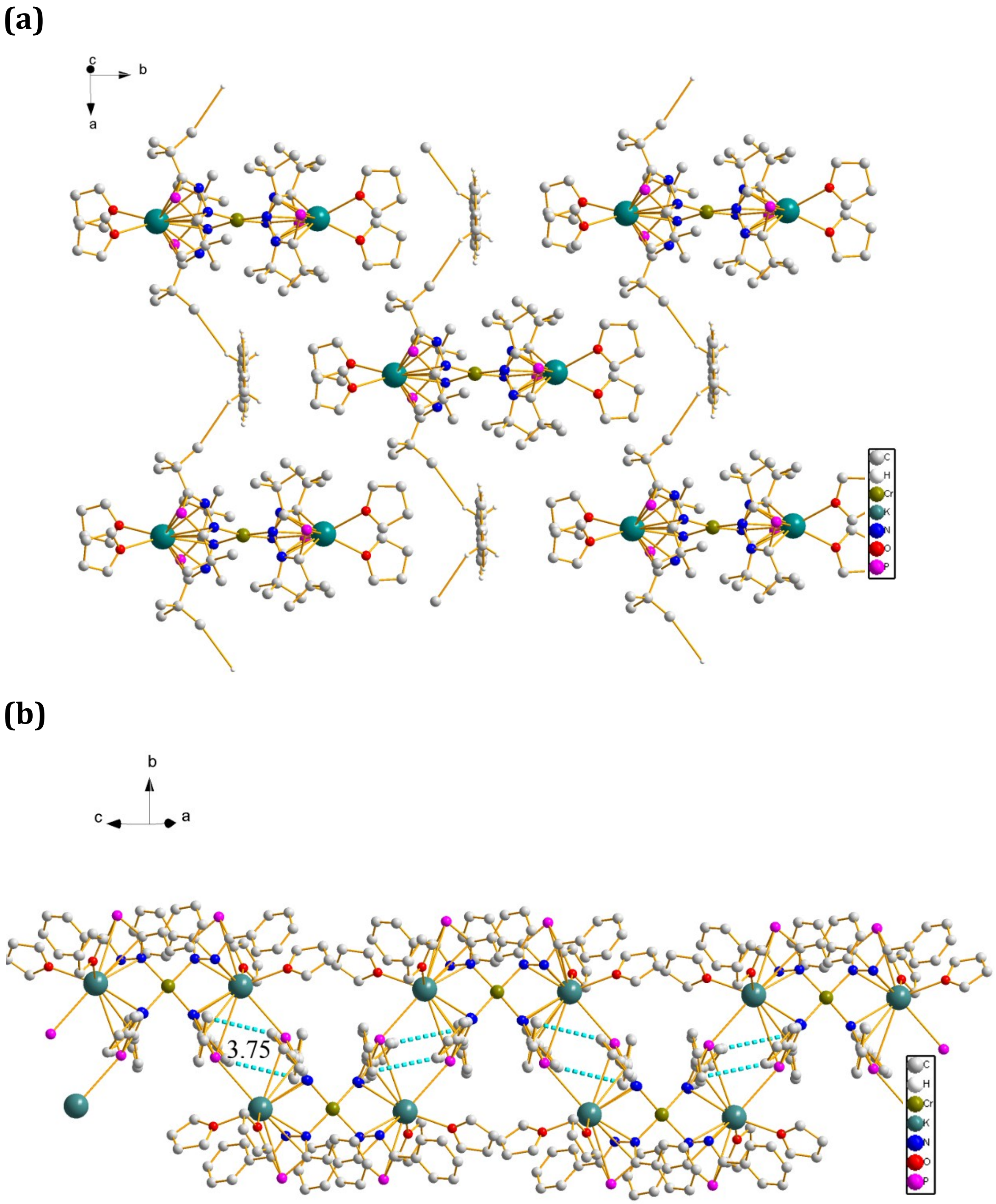

Figure ESI-3-3. (a) Packing arrangement of **5** along the crystallographic *a*, *b* axis. Hydrogen atoms in **5** omitted for clarity; (b) Packing arrangement of **6** along the crystallographic *c* axis. The dashed lines show the nearest intermolecular C(Ph)⋯C(Ph) separation (distance in Å). Hydrogen atoms omitted for clarity.

ESI-4. Magnetic Data

The magnetic properties of compound **5** was measured on powdered microcrystalline samples sealed in nitrogen-filled a 5 mm diameter quartz tube with Quantum Design SQUID MPMSXL-7 magnetometer. Dc susceptibility measurements were collected in the temperature range 2-300 K under a dc field of 1000 Oe. Dc magnetization measurements were obtained at 2 K under dc fields up to 7 T. Ac susceptibility measurements were performed at frequencies between 1 and 1218 Hz with an ac field of 2.0 Oe. Diamagnetic corrections were calculated from Pascal constants during the determination of magnetic susceptibility.

Table ESI-4-1. The best results fitted for **5** under 2000 Oe dc field by a generalized Debye model.

T/K	τ/s	α
2.0	2.56×10^{-4}	0.28
2.1	2.19×10^{-4}	0.24
2.2	1.90×10^{-4}	0.21
2.4	1.45×10^{-4}	0.15
2.5	1.29×10^{-4}	0.13
2.6	1.13×10^{-4}	0.11
2.7	1.00×10^{-4}	0.09
2.8	9.00×10^{-5}	0.08
2.9	8.02×10^{-5}	0.69
3.0	7.12×10^{-5}	0.65
3.1	6.25×10^{-5}	0.60

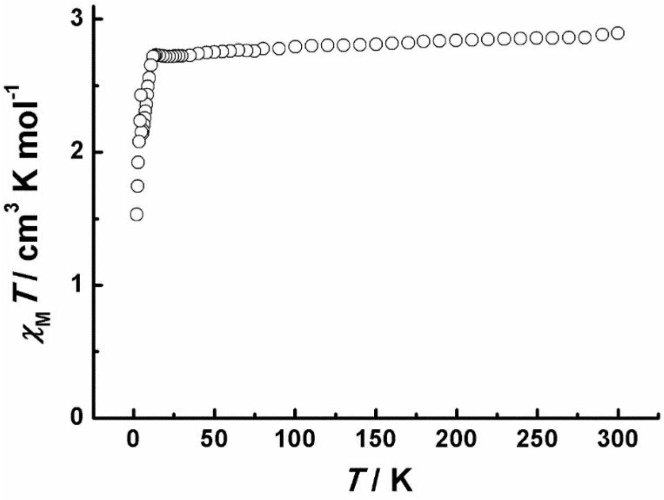

Figure ESI-4-1. $\chi_M T$ versus T plots for **5** under 1000 Oe dc field.

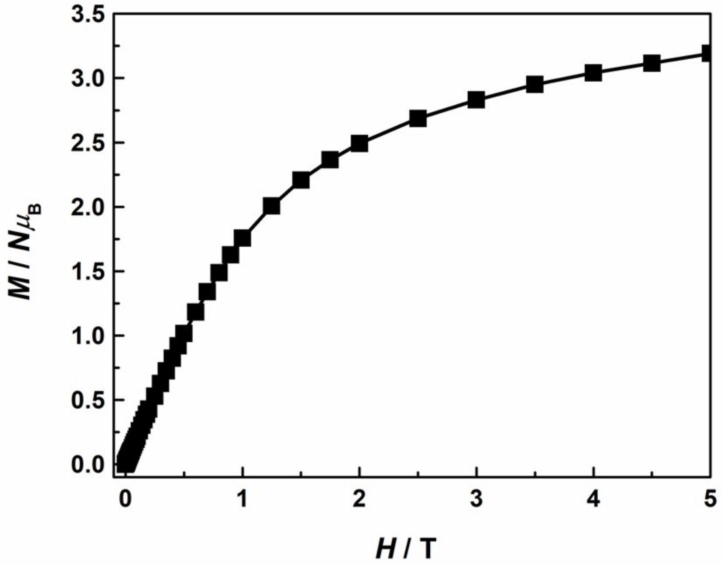

Figure ESI-4-2. Field dependence of the magnetization M at 2 K for **5.** The lines are guides to the eyes.

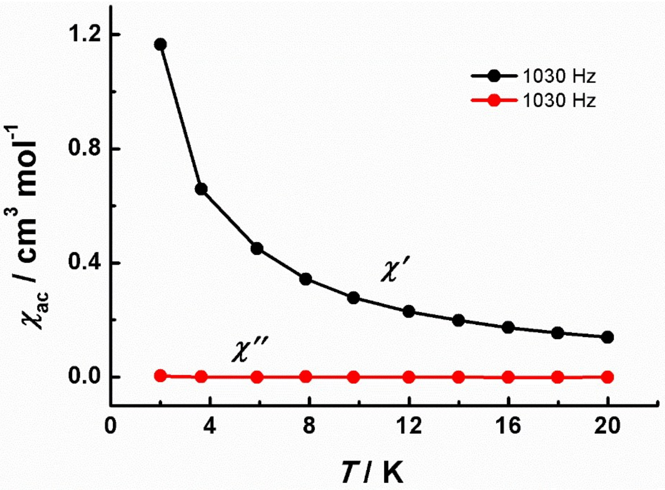

Figure ESI-4-3. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility for **5** under 0 Oe dc field. The lines are guides to the eyes.

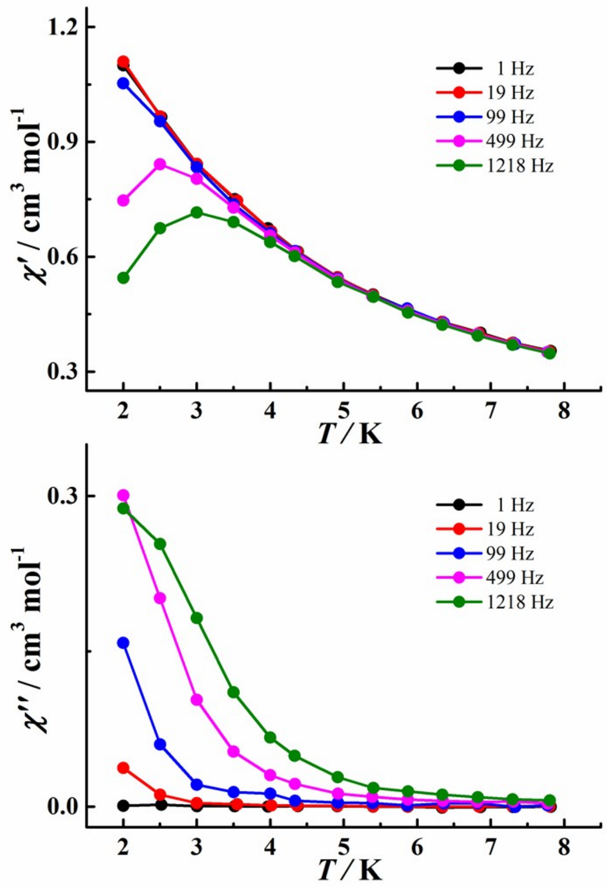

Figure ESI-4-4. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility for **5** under 2000 Oe dc field. The lines are guides to the eyes.

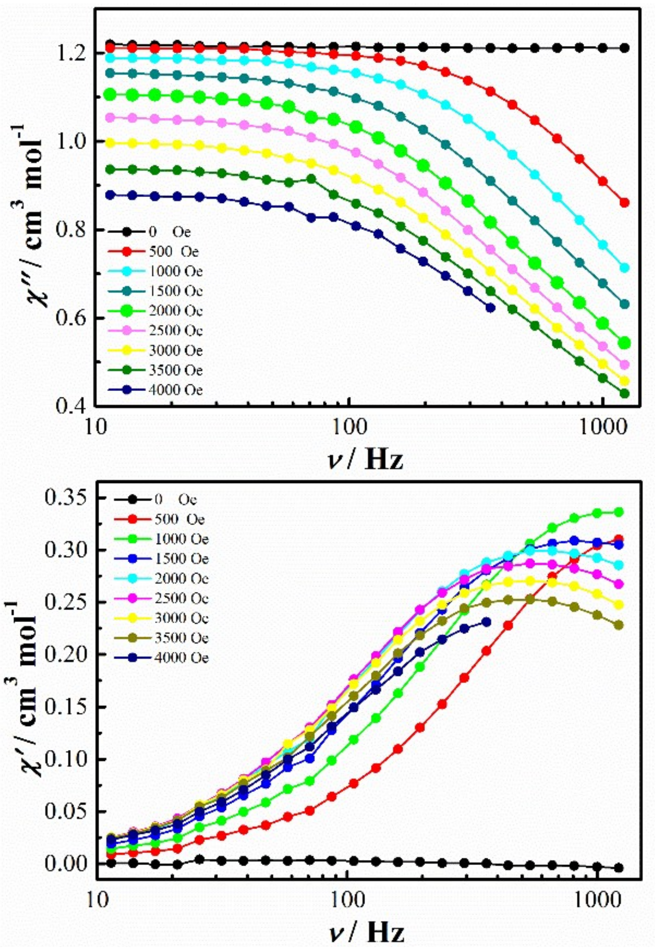

Figure ESI-4-5. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility for **5** at 2 K under various dc fields. The lines are guides to the eyes.

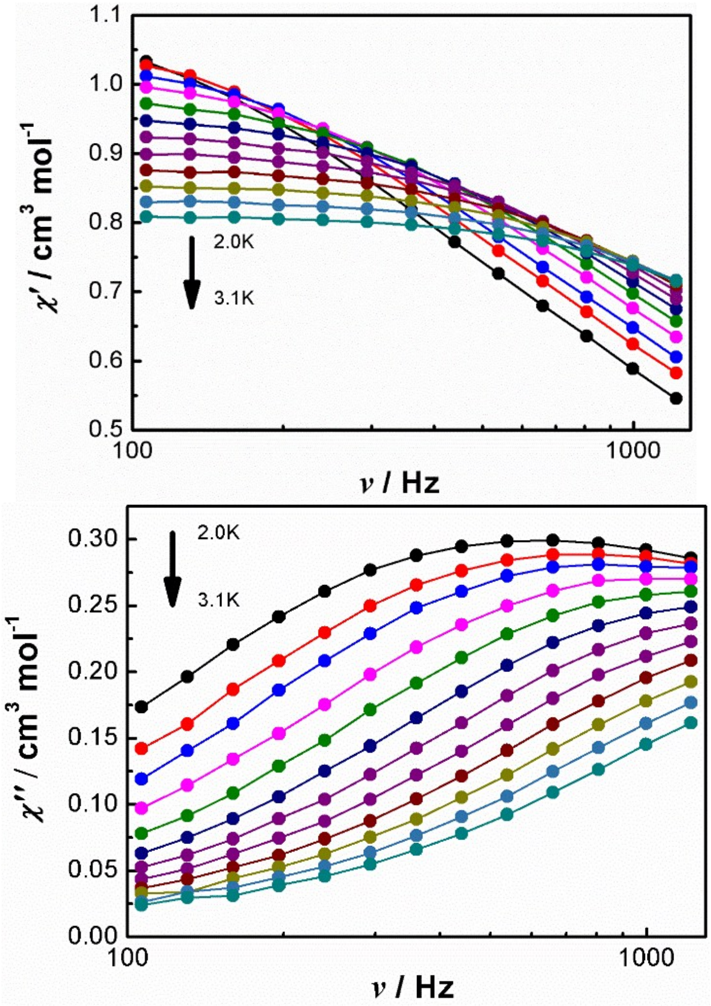

Figure ESI-4-6. Frequency dependence of the in-phase χ' (top) and out-of-phase χ'' (bottom) components of the alternating-current (ac) susceptibility for the complex **5** measured under 2000 Oe dc field in the temperature range of 2.0–3.1 K. The lines are guides to the eyes.

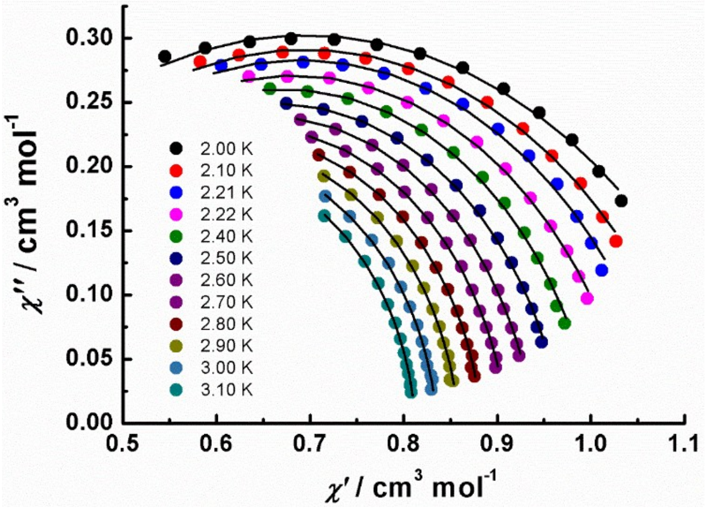

Figure ESI-4-7. Cole-Cole plots for **5** at 2000 Oe dc field. The solid lines represent a fit to the data.

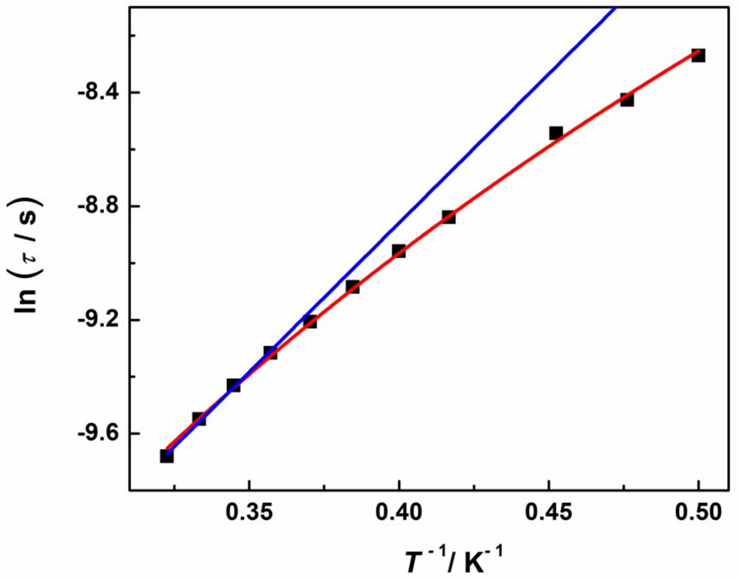

Figure ESI-4-8. Arrhenius plot of τ data for **5**. The solid line represents the best fit to Arrhenius Law.

ESI-5. HF-EPR Measurements

HF-EPR measurements were performed on a locally developed spectrometer at Wuhan National High Magnetic Field Centre, using a pulsed magnetic field of up to 30 T. The raw spectra were obtained in an absorptive mode. Simulations and fitting were performed by the SPIN program developed by Dr. Andrzej Ozarowski at the National High Magnetic Field Laboratory in Tallahassee, Florida (ozarowsk@magnet.fsu.edu).

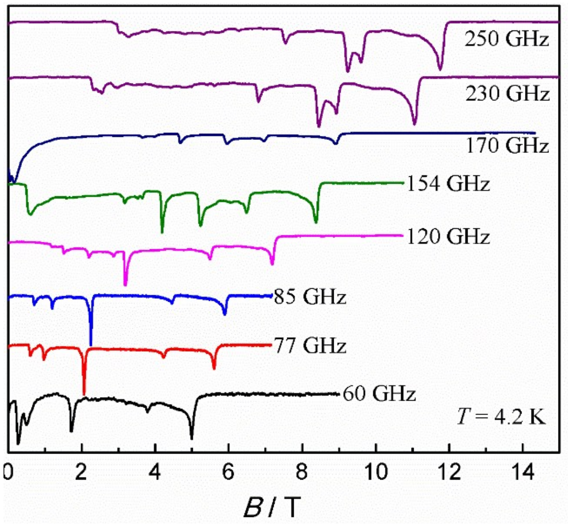

Figure ESI-5-1. Variable-frequency EPR spectra collected on a powder sample of **5** at 4.2 K.

ESI-6. The IR data for 5 and 6

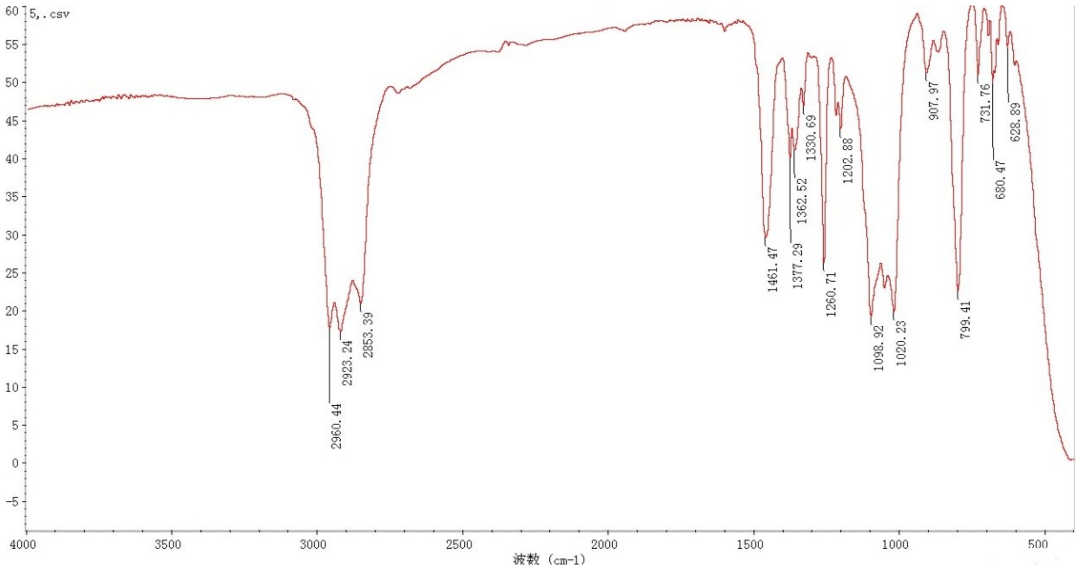

Figure ESI-6-1. The IR data for **5**

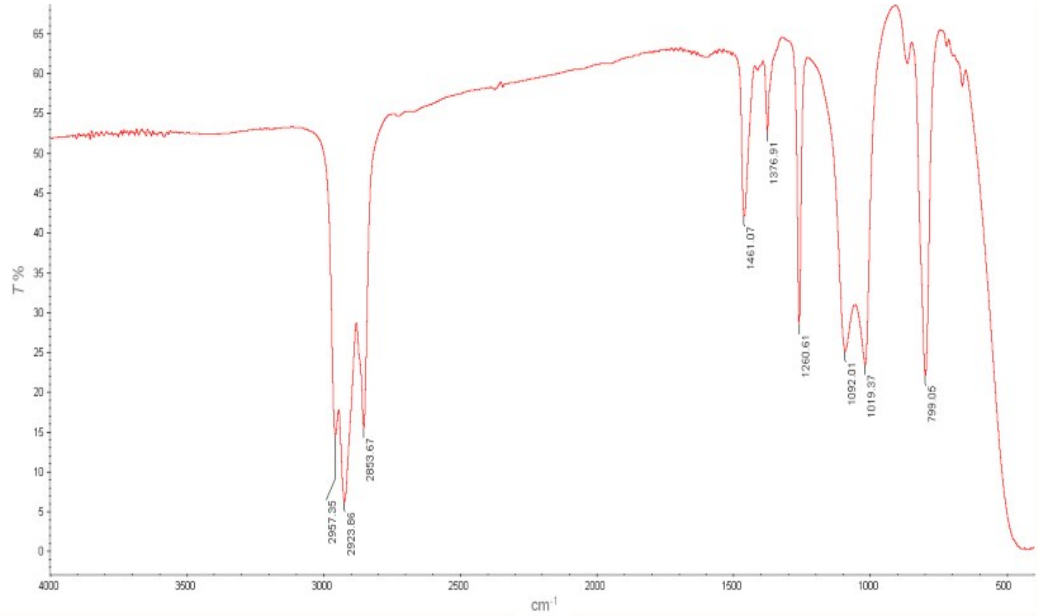

Figure ESI-6-2. The IR data for **6**