Supporting Information for:

Inspiration from old molecules: Field-induced slow magnetic relaxation in three air-stable tetrahedral cobalt(II) compounds

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Full Experimental Details

All reagents and solvents were commercially available and were used without further purification.

All manipulations were carried out at room temperature under atmosphere environment.

Preparation of dichloro bis(triphenylphosphino) cobalt(II), [Co(PPh₃)₂Cl₂] (1):

Co(PPh₃)₂Cl₂ was prepared according to a modified procedure reported in literature:¹

To a solution of triphenylphosphine (52 mg, 0.2 mmol) in CH₂Cl₂ (2.5 mL) was added a solution of CoCl₂•6H₂O (24 mg, 0.1 mmol) in MeCN (2.5 mL). The blue mixture was stirred for 2 hours and then filtered. The filtrate was allowed to stand at room temperature, and blue crystals of **1** were obtained in two days. Yield 85%. IR (KBr, cm⁻¹): 3059(m), ,1584(w), 1476(s), 1433(s), 1314(w), 1195(m), 1093(s), 1029(m), 1000(m), 744(s), 700(s), 518(s), 500(s). Elemental analysis calcd for C₁₈H₁₅ClCo_{0.5}P: C, 66.07; H, 4.62%. Found: C, 66.21; H, 4.53%.

Preparation of 2,2'-bis(diphenylphosphino)diphenyl ether dichloro cobalt(II), [Co(DPEphos)Cl₂] (2):

Co(DPEphos)Cl₂ was prepared according to a modified procedure reported in literature:²

To a solution of 2,2'-bis(diphenylphosphino)diphenyl ether (54 mg, 0.1 mmol) in CH₂Cl₂ (2.5 mL) was added a solution of CoCl₂•6H₂O (24 mg, 0.1 mmol) in MeCN (2.5 mL). The blue mixture was stirred for 2 hours and then filtered. The filtrate was allowed to stand at room temperature, and blue crystals of **2** were obtained in two days. Yield 90%. IR (KBr, cm⁻¹): 3059(m), 1574(m), 1465(s), 1433(s), 1269(m), 1226(s), 1107(m), 879(w), 750(s), 699(s), 511(s), 480(m). Elemental analysis calcd for $C_{36}H_{28}Cl_2CoOP_2+1.5$ CH₃CN: C, 64.17; H, 4.49; N, 2.88%. Found: C, 64.43; H, 4.35; N, 2.61%.

Preparation of 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene dichloro cobalt(II), [Co(Xantphos)Cl₂] (3): Co(Xantphos)Cl₂ was prepared according to a modified procedure reported in literature:²

To a solution of 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (29 mg, 0.05 mmol) in CH₂Cl₂ (2.5 mL) was added a solution of CoCl₂•6H₂O (12 mg, 0.05 mmol) in MeCN (2.5 mL). The blue mixture was stirred for half an hour and then filtered. The filtrate was allowed to stand at room temperature, and blue crystals of **3** were obtained in two days. Yield 90%. IR (KBr, cm⁻¹): 3058(m), 2974(m), 2926(w), 1563(w), 1487(m), 1422(s), 1411(s), 1248(s), 1102(m), 880(m), 750(s), 696(s), 512(s), 470(m). Elemental analysis calcd for C₃₁₂H₂₅₆Cl₁₆Co₈O₈P₁₆: C, 66.12; H, 4.55%. Found: C, 66.25; H, 4.43%.

X-ray Structure Determination. Suitable single crystals for **1-3** were glued onto a glass fiber. Diffraction intensity data for the three compounds were carried out on a Bruker Smart CCD diffractometer equipped with graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data sets were collected with the ω -scan technique and reduced by CrystalClear software. The structures of the three compounds were solved by direct methods and refined with the full-matrix leastsquares technique using the program SHELXTL.³ The location of metal atom was easily determined, and O, P, Cl, and C atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The disordered atoms were refined with constrained dimensions. The hydrogen atoms were set in calculated positions.

General Characterization and Magnetic Measurements. Elemental analyses of C, H, and N were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra as KBr pellets were recorded using reflectance technique over the range of 4000-400 cm-1 on a Magna 750 FT-IR spectrophotometer. X-ray powder diffraction (XRPD) data were recorded at room temperature on

a SHIMADZU XRD-6000 X-ray Powder Diffractometer.

The magnetic measurements of the compounds were carried out by use of a Quantum Design SQUID MPMS-VSM magnetometer. Samples were fixed in gelatin capsules and held in a brass sample holder. The temperature dependence of the dc magnetic susceptibilities were collected in the temperature range 2-300 K under a dc field of 5000 Oe. The isothermal field dependence of magnetizations were collected at 1.8 K from 0 T to 5 T. Alternating current magnetic susceptibility measurements were performed in the temperature range 1.8-4.0 K under a 3 Oe ac field oscillating at frequencies of 1-834 Hz, under an applied dc field of 0 and 1000 Oe. Dc magnetic susceptibility data were corrected for diamagnetic contributions from the sample holder, the gelatin capsule, and the core diamagnetism of each sample.

Computational details. CASSCF/CASPT2/RASSI calculations on model structures of individual molecule of the three compounds have been carried out with MOLCAS 7.6 Program package. The basis sets for all atoms were atomic natural orbitals from the MOLCAS ANO-RCC library.

	1	2	3
molecular formula	$C_{18}H_{15}ClCo_{0.5}P$	$C_{36}H_{28}Cl_2CoOP_2$	$C_{312}H_{256}Cl_{16}Co_8O_8P_{16}$
formula weight	327.19	668.35	5667.33
temperature	293(2) K	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic	Monoclinic
space group	P2/c	$P2_{1}/c$	$P2_{1}/c$
<i>a</i> / Å	11.7637(5)	11.6119(7)	17.021(3)
<i>b</i> / Å	8.2529(6)	19.3669(15)	10.623(2)
c / Å	17.2302(9)	18.2530(14)	40.440(11)
β / deg	106.419(3)	122.107(5)	111.06(3)
$V/\text{\AA}^3$	1604.57(16)	3477.0(4)	6824(3)
Z	4	4	1
$D_{calc}, \mathrm{g/cm}^3$	1.354	1.277	1.379
μ	0.825 mm^{-1}	0.765 mm ⁻¹	0.784 mm ⁻¹
<i>F</i> (000)	674	1372	2920
GOF on F^2	1.030	1.200	0.969
final <i>R</i> indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0271$	$R_1 = 0.0343$	$R_1 = 0.0560$
	$wR_2 = 0.0663$	$wR_2 = 0.0573$	$wR_2 = 0.1008$
R indices (all data)	$R_1 = 0.0349$	$R_1 = 0.1098$	$R_1 = 0.1476$
	$wR_2 = 0.0714$	$wR_2 = 0.2173$	$wR_2 = 0.1256$

Table S1. Crystal Data and Structure Determination Summarise for 1, 2, and 3

^a $R_I = ||F_0| - |F_c|| / \sum |F|_0$. ^b $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_0^2) + (ap)^2 + (bp)]$, $p = [max(F_0^2, 0) + 2(F_c^2)]/3$.

	1	2	3
Co1-Cl1	2.2109(6)	2.2173(7)	2.2403(13)
Co1-Cl2		2.2231(8)	2.2079(14)
Co1-P1	2.3858(5)	2.4185(7)	2.3882(11)
Co1-P2		2.4215(7)	2.3955(12)
Cl2-Co1-Cl1	117.12(4)	112.90(3)	117.41(6)
Cl2-Co1-P1	107.308(19)	102.84(3)	108.21(5)
Cl1-Co1-P2		106.59(3)	106.52(4)
Cl1-Co1-P1	104.86(2)	109.32(3)	103.54(4)
Cl2-Co1-P2		112.86(3)	107.98(5)
P1-Co1-P2	115.86(3)	112.41(2)	113.33(4)

Table S2. Summar	y of bond length (A	Å) and Angles	(deg) for the X-ray	structures of 1, 2, and 3
	2 0 1	/ 0		, , ,



Figure S1. Packing arrangement of 1 along the crystallographic *b* axis.



Figure S2. Packing arrangement of 2 along the crystallographic *a* axis.



Figure S3. Packing arrangement of 3 along the crystallographic *b* axis.



Figure S4. XRPD pattern for compound 1.



Figure S5. XRPD pattern for compound 2.



Figure S6. XRPD pattern for compound 3.



Fig. S7 Magnetic susceptibility of the compounds plotted as $\chi_M T$ vs T curves. For **2**, the slight increase in $\chi_M T$ above 250 K is reproducible and could be due to a structural phase transition as has been observed in the past.^{4,5}



Fig. S8 The isothermal field dependence of magnetization at 1.8 K for the compounds.



Fig. S9 Low-temperature magnetization data for 1 collected under various applied dc fields. The solid lines represent fits to the data.



Fig. S10 Low-temperature magnetization data for 3 collected under various applied dc fields. The solid lines represent fits to the data.



Fig. S11 Temperature dependence of out-of-phase (χ'') ac susceptibility component at different ac frequency ($H_{ac} = 3$ Oe and $H_{dc} = 1000$ Oe) for **1**.



Fig. S12 Frequency dependence of the out-of-phase ac susceptibility from 2.1 to 3.2 K under 1000 Oe dc field for **1**.



Fig. S13 Cole-Cole plot of 1 under 1000 Oe at temperatures between 2.4 K (red) and 3.2 K (black); the solid lines are the best fit obtained with a generalized Debye model (with α always smaller than 0.02).



Fig. S14 Relaxation time of the magnetization $\ln(\tau)$ vs T^1 plot of **1**; the solid line correspond to the Arrhenius law.



Fig. S15 Temperature dependence of out-of-phase (χ'') ac susceptibility component at different ac frequency ($H_{ac} = 3$ Oe and $H_{dc} = 1000$ Oe) for **3**.

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Fig. S16 Frequency dependence of the out-of-phase ac susceptibility from 2.1 to 3.2 K under 1000 Oe dc field for **3**.



Fig. S17 Cole-Cole plot of 3 under 1000 Oe at temperatures between 2.0 K (red) and 3.3 K (black); the solid lines are the best fit obtained with a generalized Debye model (with α always smaller than 0.05).



Fig. S18 Relaxation time of the magnetization $\ln(\tau)$ vs T^1 plot of **3**; the solid line corresponds to the Arrhenius law.

References

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