

## Supporting information

### **Polar metal phosphonate containing unusual $\mu_4$ -OH bridged double chains showing canted antiferromagnetism with large coercivity**

Xiao-Jing Yang, Song-Song Bao, Min Ren, Norihisa Hoshino, Tomoyuki Akutagawa and Li-Min Zheng\*

**Materials and methods.** Ethyl o-toluate (98+%) and other materials of analytical grade were obtained from commercial sources and used without further purification. The 2-(phosphonomethyl)benzoic acid (2-pmbH<sub>3</sub>) was prepared according to the literature.<sup>1</sup> Elemental analyses for C, H were performed on an Elementar Vario MICRO elemental analyzer. The infrared spectra were recorded on a Bruker VECTOR 22 IR spectrometer with pressed KBr pellets in the 400–4000 cm<sup>-1</sup> region. Thermogravimetric analyses were performed on a METTLER TOLEDO TGA/DSC 1 instrument in the range of 30-800 °C under a nitrogen flow at a heating rate of 10 °C min<sup>-1</sup>. Powder X-ray diffraction patterns were recorded on a SHIMADZU XRD-6000 instrument using Cu-K $\alpha$  radiation. Liquid state <sup>1</sup>H NMR spectrum was recorded at room temperature on a Bruker Advance DPX 500 spectrometer. The magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design MPMSXL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants.<sup>2</sup> The magnetization curves at different temperatures were recorded on a vibrating sample magnetometer (VSM) of Quantum Design-MPMS-SQUID-VSM system.

**Synthesis of Co<sub>2</sub>( $\mu_4$ -OH)(2-pmb) (1).** Compound **1** was obtained as purple needle-like crystals by hydrothermal treatment of a mixture of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.0199 g, 0.20 mmol), 2-pmbH<sub>3</sub> (0.0216 g, 0.1 mmol) and 8 mL H<sub>2</sub>O (pH 7.35 adjusted by 0.5 M NaOH) at 160 °C for 48 h. Yield: 0.0150 g (70% based on Co). Elemental analysis calcd. for C<sub>8</sub>H<sub>7</sub>O<sub>6</sub>PCo<sub>2</sub>: C, 27.59; H, 2.01. Found: C, 27.47; H, 2.07%. IR (KBr, cm<sup>-1</sup>): 3549.2(s), 3415.9(br, m), 1602.7(s), 1584.3(s), 1555.0(s), 1445.7(w), 1410.3(m), 1381.1(vs), 1242.6(m), 1166.3(w), 1141.3(w), 1090.6(s), 1035.6(vs), 996.4(m), 808.1(w), 780.6(w), 725.4(m), 711.6(w), 665.7(w), 608.3(w), 562.4(m), 527.9(w), 491.1(w), 463.6(w), 426.9(w).

**Synthesis of Cu<sub>4</sub>( $\mu_3$ -OH)<sub>2</sub>(2-pmb)<sub>2</sub> (2).** Compound **2** was obtained similarly except that Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O instead of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was used as the starting material and the pH is 4.80. Blue plate-like crystals were collected as a monophasic material with a yield of 0.0150 g (83% based on Cu). Elemental analysis calcd. for

C<sub>16</sub>H<sub>14</sub>O<sub>12</sub>P<sub>2</sub>Cu<sub>4</sub>: C, 26.88; H, 1.96. Found: C, 26.68; H, 1.95 %. IR (KBr, cm<sup>-1</sup>): 3523.8(m), 3407.5(br,m), 1600.5(w), 1578.1(m), 1541.2(vs), 1488.5(w), 1454.3(m), 1425.3(m), 1410.8(m), 1237.3(w), 1162.6(m), 1133.8(m), 1080.4(vs), 1005.7(s), 875.8(w), 840.2(w), 830.5(w), 791.7(w), 747.4(m), 716.9(w), 676.7(w), 622.7(w), 589.5(w), 578.4(w), 498.0(w), 466.2(m), 417.7(m).

**Crystallographic studies.** Single crystals of dimensions 0.2 x 0.05 x 0.05 mm<sup>3</sup> for **1** and 0.4 x 0.1 x 0.1 mm<sup>3</sup> for **2** were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. A hemisphere of data were collected in the  $\theta$  range 2.90–24.97° for **1** and 2.73–25.00° for **2**, respectively, using a narrow-frame method with scan widths of 0.30° in  $\omega$  and an exposure time of 5 s/frame. The data were integrated using the Siemens SAINT program,<sup>3</sup> with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector face plate. Absorption corrections were applied. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using SHELXTL.<sup>4</sup> All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically with the isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. The crystallographic data are listed in Table S1, and the selected bond lengths and angles are given in Tables S2 and S3.

## References

- (1) Kaur, K.; Lan, M. J. K.; Pratt, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 10436-10443.
- (2) Kahn, O. *Molecular Magnetism*. New York, VCH Publishers, **1993**.
- (3) *SAINT, Program for Data Extraction and Reduction*, Siemens Analytical X-ray Instruments, Madison, WI, **1994–1996**.
- (4) *SHELXTL (version 5.0), Reference Manual*, Siemens Industrial Automation, Analytical Instruments, Madison, WI, **1995**.

**Table S1.** Crystallographic data for **1-2**.

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>8</sub> H <sub>7</sub> O <sub>6</sub> PCO <sub>2</sub>	C <sub>16</sub> H <sub>14</sub> Cu <sub>4</sub> O <sub>12</sub> P <sub>2</sub>
Fw	347.97	714.37
Crystal size / mm <sup>3</sup>	0.2 x 0.05 x 0.05	0.4 x 0.1 x 0.1
Crystal system	Monoclinic	Orthorhombic
Space group	<i>Cc</i>	<i>Pca2<sub>1</sub></i>
<i>a</i> / Å	7.3437(19)	9.917(6)
<i>b</i> / Å	24.282(6)	7.450(4)
<i>c</i> / Å	5.3533(14)	28.101(16)
$\beta$ / °	93.061(4)	
<i>V</i> / Å <sup>3</sup>	953.2(4)	2076(2)
<i>Z</i>	4	4
$\rho_c$ / g cm <sup>-3</sup>	2.425	2.285
Absorption coefficient/mm <sup>-1</sup>	3.660	4.262
F(000)	688	1408
Theta range for data collection / °	2.90 to 24.97	2.73 to 25.00
Reflections collected/unique	2366/1563 (R <sub>int</sub> = 0.0363)	9685/3433 (R <sub>int</sub> = 0.0959)
Max. and min. transmission	0.883 and 0.481	0.653 and 0.180
Data / restraints / parameters	1563 / 2 / 154	3433 / 43 / 308
Goodness-of-fit on F <sup>2</sup>	1.005	0.952
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0341, 0.0698	0.0437, 0.0993
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (All data) <sup>a</sup>	0.0367, 0.0705	0.0552, 0.1038
Absolute structure parameter	0.02(3)	0.59(3)
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> / e Å <sup>-3</sup>	0.515, -0.455	1.144, -0.676

<sup>a</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ .  $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{3}$ .

**Table S2.** Selected bond lengths [ $\text{\AA}$ ] and angles [deg] for **1<sup>a</sup>**.

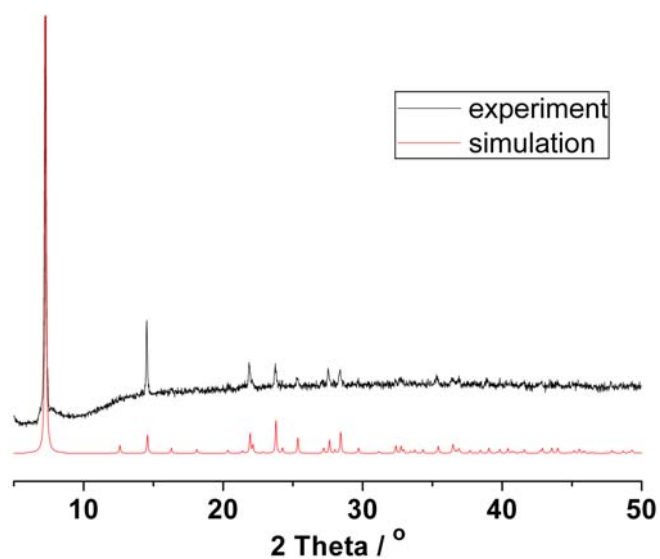
Co(1) – O(1)	2.027(4)	Co(2) – O(3)	2.014(4)
Co(1) – O(2A)	2.062(4)	Co(2) – O(3E)	2.004(4)
Co(1) – O(5B)	2.073(5)	Co(2) – O(4)	2.247(4)
Co(1) – O(2C)	2.111(4)	Co(2) – O(4A)	2.037(4)
Co(1) – O(6B)	2.217(5)	Co(2) – O(6)	2.073(4)
Co(1) – O(6D)	2.255(4)	Co(2) – O(6A)	2.241(5)
P(1) – O(1)	1.511(4)	P(1) – O(2)	1.539(4)
P(1) – O(3)	1.533(5)		
O(1)-Co(1)-O(2A)	89.80(18)	O(3E)-Co(2)-O(3)	104.2(2)
O(1)-Co(1)-O(2C)	109.26(17)	O(3E)-Co(2)-O(4A)	102.35(18)
O(1)-Co(1)-O(5B)	92.74(19)	O(3)-Co(2)-O(4A)	85.93(17)
O(1)-Co(1)-O(6B)	168.39(17)	O(3E)-Co(2)-O(6)	88.29(17)
O(1)-Co(1)-O(6D)	89.09(17)	O(3)-Co(2)-O(6)	158.5(2)
O(2A)-Co(1)-O(2C)	97.49(16)	O(4A)-Co(2)-O(6)	108.74(19)
O(2A)-Co(1)-O(5B)	174.18(17)	O(3E)-Co(2)-O(6A)	171.88(17)
O(2A)-Co(1)-O(6B)	84.49(18)	O(3)-Co(2)-O(6A)	83.55(18)
O(2A)-Co(1)-O(6D)	81.71(18)	O(4A)-Co(2)-O(6A)	80.35(17)
O(2C)-Co(1)-O(6B)	81.57(17)	O(6)-Co(2)-O(6A)	83.59(17)
O(2C)-Co(1)-O(6D)	161.65(15)	O(3E)-Co(2)-O(4)	80.79(17)
O(5B)-Co(1)-O(2C)	86.62(19)	O(3)-Co(2)-O(4)	85.28(17)
O(5B)-Co(1)-O(6B)	92.07(18)	O(4A)-Co(2)-O(4)	171.16(19)
O(5B)-Co(1)-O(6D)	93.08(18)	O(6)-Co(2)-O(4)	79.46(17)
O(6B)-Co(1)-O(6D)	80.10(14)	O(6A)-Co(2)-O(4)	97.69(17)
P(1)-O(1)-Co(1)	129.1(3)	P(1)-O(3)-Co(2A)	143.4(3)
P(1)-O(2)-Co(1E)	118.9(3)	P(1)-O(3)-Co(2)	132.1(3)
P(1)-O(2)-Co(1F)	140.4(3)	Co(2A)-O(3)-Co(2)	84.38(17)
Co(1E)-O(2)-Co(1F)	100.56(18)	Co(2E)-O(4)-Co(2)	77.93(14)
Co(2)-O(6)-Co(1G)	130.2(2)	Co(2)-O(6)-Co(2E)	77.32(15)
Co(1G)-O(6)-Co(2E)	89.15(18)	Co(2)-O(6)-Co(1H)	92.50(17)
Co(1G)-O(6)-Co(1H)	91.73(17)	Co(2E)-O(6)-Co(1H)	167.3(2)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: (A)  $x, -y, z-1/2$ ; (B)  $x+1, y, z-1$ ; (C)  $x, y, z-1$ ; (D)  $x+1, -y, z-1/2$ ; (E)  $x, -y, z+1/2$ ; (F)  $x, y, z+1$ ; (G)  $x-1, y, z+1$ ; (H)  $x-1, -y, z+1/2$ .

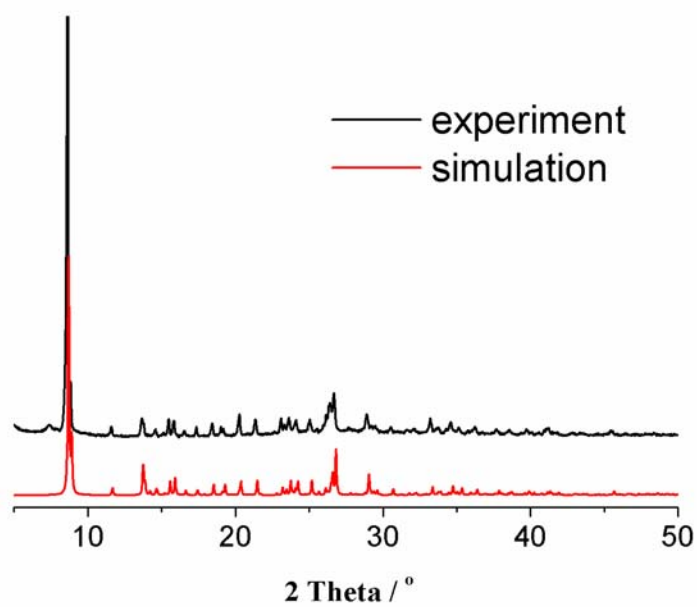
**Table S3.** Selected bond lengths [ $\text{\AA}$ ] and angles [deg] for **2**<sup>a</sup>.

Cu(1) – O(1A)	1.942(7)	Cu(3) – O(2)	1.982(7)
Cu(1) – O(3A)	1.929(7)	Cu(3) – O(11)	1.988(6)
Cu(1) – O(8A)	2.293(6)	Cu(4) – O(9B)	1.897(7)
Cu(1) – O(11)	1.955(6)	Cu(4) – O(12)	1.991(6)
Cu(1) – O(12)	2.007(6)	Cu(4) – O(8A)	1.929(6)
Cu(2) – O(7)	1.949(6)	Cu(4) – O(6D)	1.968(7)
Cu(2) – O(10)	1.910(7)	P(1) – O(3)	1.501(7)
Cu(2) – O(4B)	2.293(6)	P(1) – O(4)	1.546(6)
Cu(2) – O(11)	2.008(6)	P(1) – O(5)	1.520(7)
Cu(2) – O(12)	1.949(6)	P(2) – O(8)	1.546(7)
Cu(3) – O(5C)	1.885(6)	P(2) – O(9)	1.522(7)
Cu(3) – O(4B)	1.933(6)	P(2) – O(10)	1.506(7)
O(1A)-Cu(1)-O(8A)	102.6(3)	O(5C)-Cu(3)-O(4B)	175.6(3)
O(1A)-Cu(1)-O(12)	171.6(3)	O(5C)-Cu(3)-O(2)	88.4(3)
O(1A)-Cu(1)-O(11)	91.5(3)	O(4B)-Cu(3)-O(2)	94.3(3)
O(3A)-Cu(1)-O(1A)	99.0(3)	O(5C)-Cu(3)-O(11)	93.9(3)
O(3A)-Cu(1)-O(8A)	92.8(3)	O(4B)-Cu(3)-O(11)	83.0(3)
O(3A)-Cu(1)-O(11)	167.4(3)	O(2)-Cu(3)-O(11)	172.6(3)
O(3A)-Cu(1)-O(12)	88.8(3)	O(9B)-Cu(4)-O(8A)	175.5(3)
O(11)-Cu(1)-O(8A)	91.5(3)	O(9B)-Cu(4)-O(6D)	87.9(3)
O(11)-Cu(1)-O(12)	81.0(2)	O(8A)-Cu(4)-O(6D)	94.8(3)
O(12)-Cu(1)-O(8A)	74.0(2)	O(9B)-Cu(4)-O(12)	93.9(3)
O(10)-Cu(2)-O(7)	99.1(3)	O(8A)-Cu(4)-O(12)	83.0(2)
O(10)-Cu(2)-O(12)	166.3(3)	O(6D)-Cu(4)-O(12)	172.2(3)
O(7)-Cu(2)-O(12)	91.9(3)	Cu(3F)-O(4)-Cu(2F)	90.5(2)
O(10)-Cu(2)-O(11)	88.3(3)	Cu(4E)-O(8)-Cu(1E)	90.5(2)
O(7)-Cu(2)-O(11)	171.9(3)	Cu(1)-O(11)-Cu(3)	119.5(3)
O(12)-Cu(2)-O(11)	81.1(2)	Cu(1)-O(11)-Cu(2)	98.8(3)
O(10)-Cu(2)-O(4B)	93.9(3)	Cu(3)-O(11)-Cu(2)	97.8(2)
O(7)-Cu(2)-O(4B)	102.3(3)	Cu(2)-O(12)-Cu(4)	119.6(3)
O(12)-Cu(2)-O(4B)	91.6(3)	Cu(2)-O(12)-Cu(1)	99.0(3)
O(11)-Cu(2)-O(4B)	74.0(2)	Cu(4)-O(12)-Cu(1)	97.6(2)

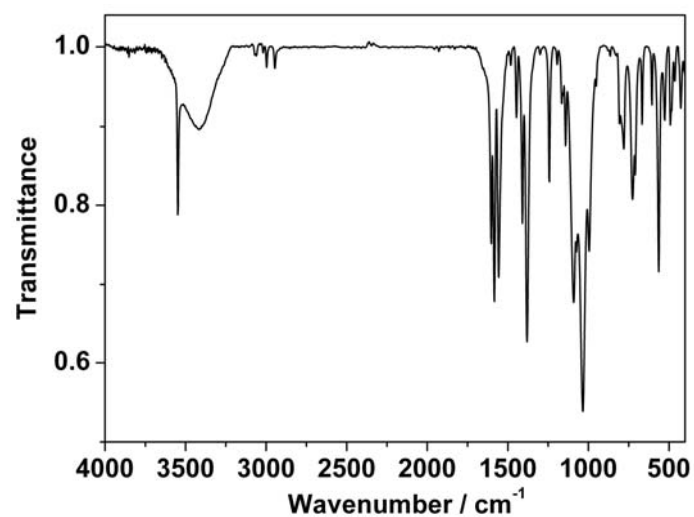
<sup>a</sup>Symmetry transformations used to generate equivalent atoms: (A)  $x-1/2, -y+1, z$ ; (B)  $x, y-1, z$ ; (C)  $x-1/2, -y+2, z$ ; (D)  $x-1/2, -y, z$ ; (E)  $x+1/2, -y+1, z$ ; (F)  $x, y+1, z$ ; (G)  $x+1/2, -y+2, z$ ; (H)  $x+1/2, -y, z$



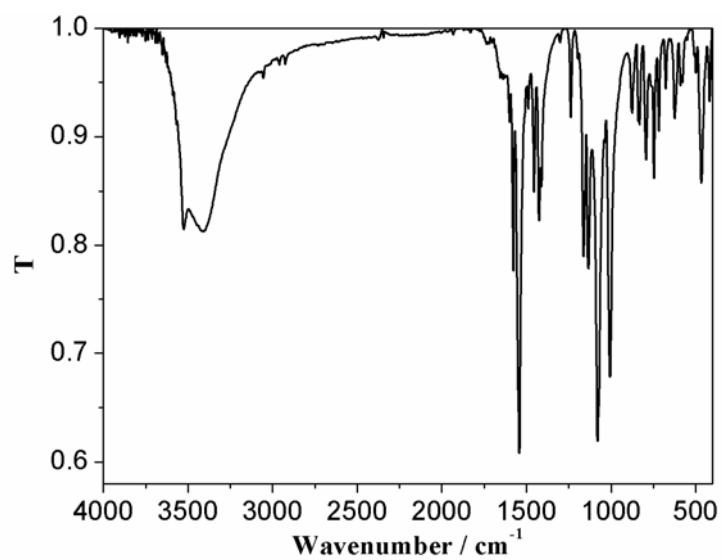
**Figure S1.** The PXRD patterns for the as-synthesized (black) and that simulated from the single crystal structural data (red) of compound **1**.



**Figure S2.** The PXRD patterns for the as-synthesized (black) and that simulated from the single crystal structural data (red) of compound **2**.

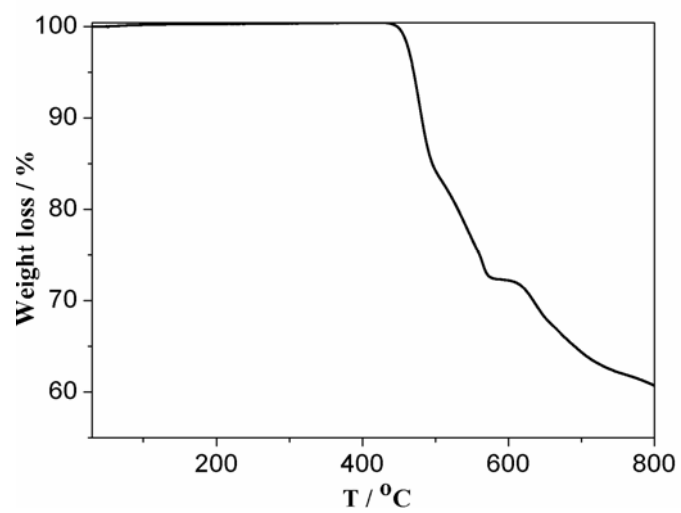


**Figure S3.** IR spectrum for compound **1** in KBr pellet.

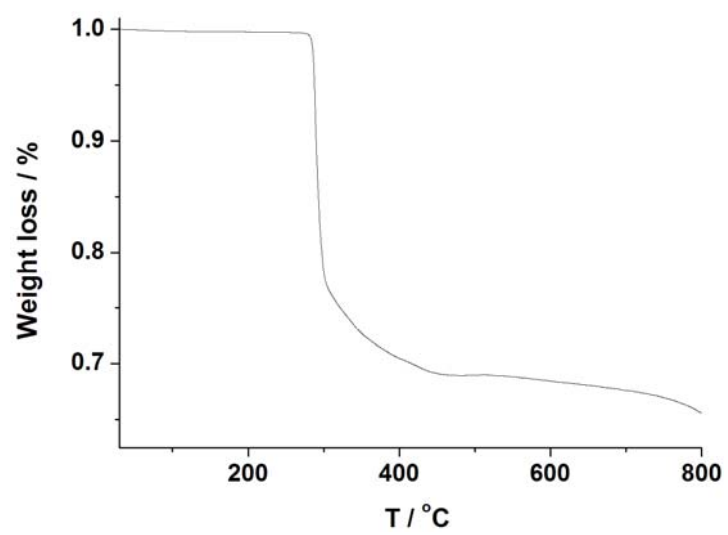


**Figure S4.** IR spectrum for compound **2** in KBr pellet.

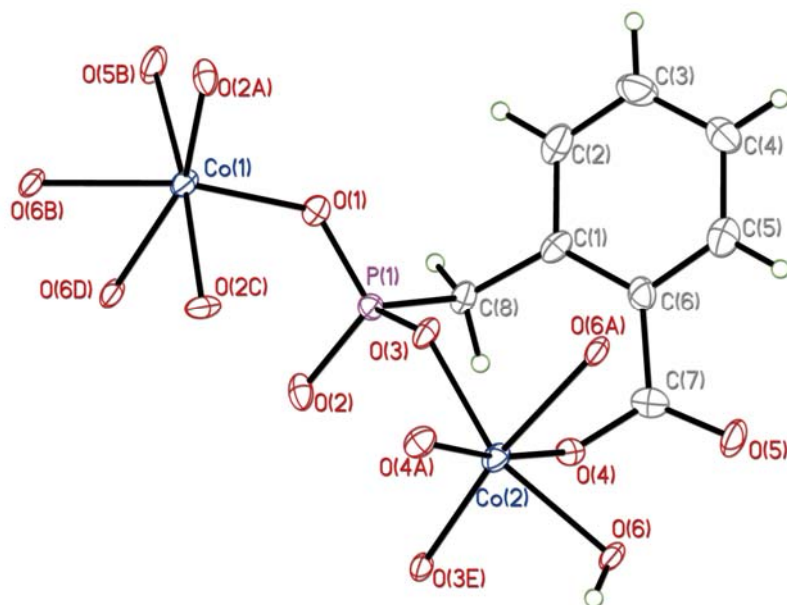




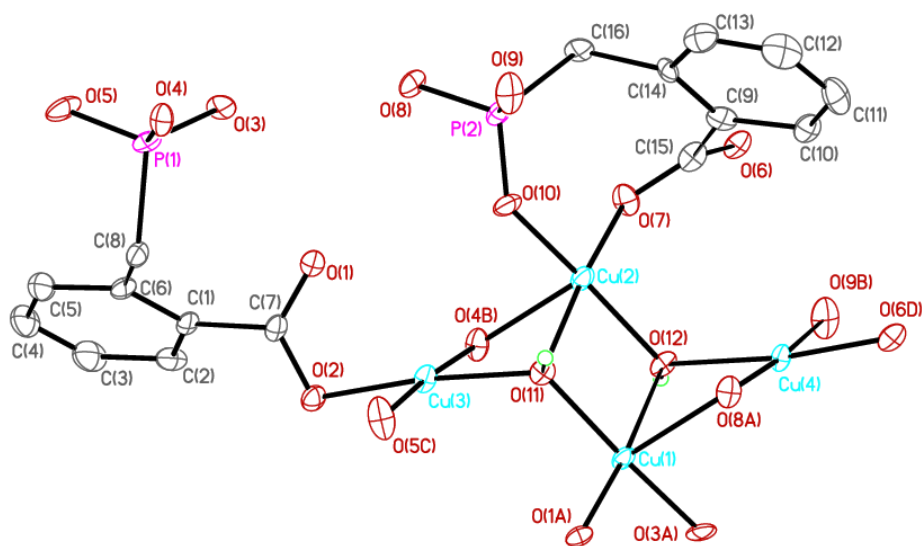
**Figure S5.** TGA curve for compound 1.



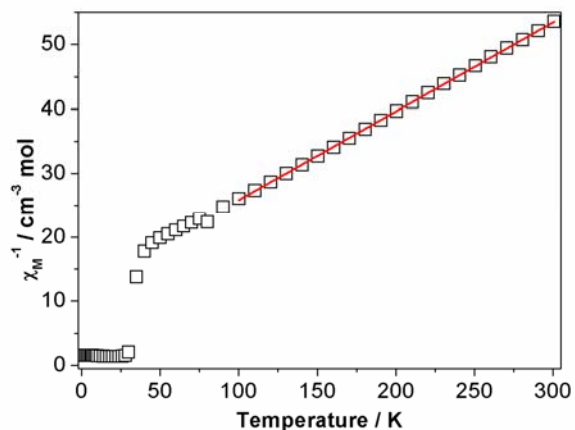
**Figure S6.** TGA curve for compound 2.



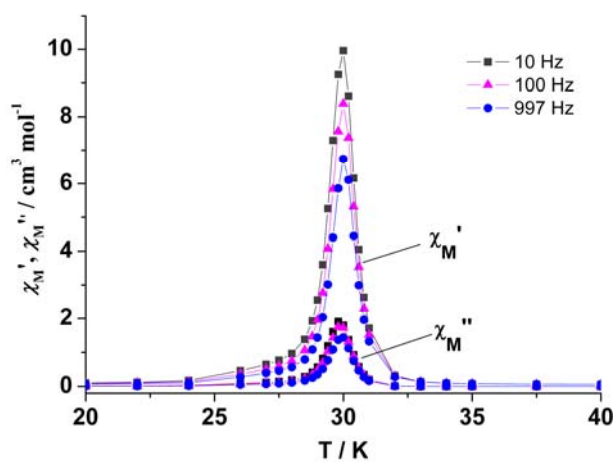
**Figure S7** Building unit of **1** with atomic labeling scheme (50% probability).



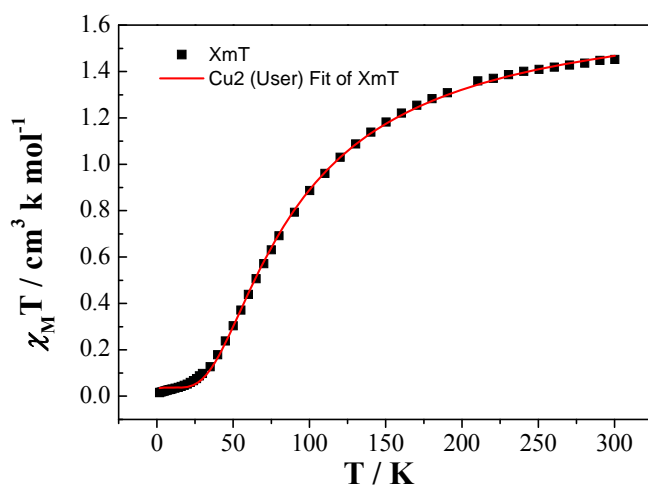
**Figure S8** Building unit of **2** with atomic labeling scheme (50% probability).



**Figure S9** The  $\chi_M^{-1}$  vs. T plot for compound **1**.



**Figure S10** Temperature dependent zero field *ac* magnetic susceptibilities of compound **1** at different frequencies ( $H_{ac} = 5$  Oe).



**Figure S11** The  $\chi_M T$  vs T plot for compound **2**.