Supporting information

Tuning the Field-induced Magnetic Transition in a Layered Cobalt Phosphonate by Reversible Dehydration-hydration Process

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Experimental details:

Preparation of 1. A mixture of $Co(OAc)_2·4H_2O$ (0.1 mmol), 2-pyridylmethylphosphonic acid[1] (0.1 mmol) in 8 mL H_2O was kept in a Teflon-lined autoclave at 140 °C for 48 h. After it is slowly cooled to room temperature, purple-red block crystals were collected as a single phase, judged by the powder X-ray diffraction measurement. Yield: 41%. Anal. Found (calcd) for $C_6H_{10}NO_5PCo$: C, 27.07 (27.09); H, 3.78 (3.79); N, 5.21 (5.26)%. IR (KBr, cm^{-1}): 3596 (m), 3439 (br), 3096 (br), 2943(w), 2365 (w), 2344(w), 1647(m), 1604 (m), 1568(m), 1478 (m), 1447 (m), 1397 (w), 1315(m), 1269(m), 1216(m), 1170 (w), 1143(s), 1116(s), 1058(s), 1018 (w), 981 (s), 836 (m), 798 (s), 766(w), 730 (m), 681 (m), 641(w), 622 (m), 572 (m), 457 (m), 422 (w).

References:

1. X.-M. Gan, I. Binyamin, B. M. Rapko, J. Fox, E. N. Duesler, R. T. Paine, *Inorg. Chem.* **2003**, *43*, 2443.

Measurements. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Thermal analyses were performed in nitrogen in the temperature range 20-700 °C with a heating rate of 10 °C/min on a TGA-DAT V101B TA Inst 2100. The powder X-ray diffraction (XRD) analyses were carried out on a Philips X'pert Pro diffractometer using Ni-filtered Cu Kα radiation (0.15418 nm). Magnetic susceptibility was measured on polycrystalline samples by using a Quantum Design MPMS-XL7 SQUID magnetometer.

Details for the powder XRD structural determination of 2 and 3. The powder XRD data for the structure determinations of (**2**) and (**3**) were collected at room temperature in Debye-Scherrer mode at the X16C beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The samples were contained in sealed lithiumborate glass capillaries with 0.5 mm diameter (Hilgenberg glass No. 50). X-rays of wavelength of approximately 0.7 Å were selected by a double Si(111) monochromator. The wavelength and zero point error have been calibrated using 8 precisely measured peaks of the NBS1976 flat plate Alumina standard. The diffracted beam was analyzed by reflection from a Ge(111) crystal before a NaI scintillation detector. Data were taken for 2.0 s. at each 2θ step of 0.005° from 3° to 35°. The samples were spun during measurement for better particle statistics. All data were normalized for storage ring current decay by an ionization chamber monitor. Further experimental details can be found in Table S1.

For indexing of the powder patterns of (**2**) and (**3**) at T = 298 K, the program TOPAS (Bruker-AXS) was used. Indexing was performed by iterative use of singular value decomposition (LSI) (Coelho, 2003), leading to primitive monoclinic unit cells with lattice parameters given in Table S1. The most probable space group could be determined as $P2_1/n$ for both phases from the observed extinction rules. The number of formula units per unit cell could be determined to Z = 4 from volume increments. Small amounts of the mono- and di-hydrate phases, respectively, were found as impurity phases in the powder patterns of (**2**) and (**3**) and were included as a so called "peaks-phases" in the refinement process. The peak profiles and precise lattice parameters of the powder patterns of (**2**) and (**3**) were first determined by a LeBail fit (LeBail, Duroy, Fourquet, 1988) using the fundamental parameter (FP) approach of TOPAS (Cheary, Coelho, Cline, 2004). A good fit to the data was obtained. The apparent anisotropic width of the peaks in the powder patterns of both phases was modeled successfully using the phenomenological microstrain model of Stephens [17] refining 9 parameters for the monoclinic case.

The crystal structures of (**2**) and (**3**) at T = 298 K were solved by the global optimization method of simulated annealing in real space using the TOPAS program.

The atomic positions of all non-hydrogen atoms of (**3**) (6 carbon atoms, 1 nitrogen atom, 3 oxygen atom, 1 sulphur atom and 1 cobalt atom) were subjected to global optimization without any constraints. Only two of the atomic positions were assigned to the wrong atom type. The structure giving the best fit to the data in space group $P2_1/n$ was validated by Rietveld refinement using the TOPAS program. Two isotropic temperature factors for the pmp-2 molecule and for the cobalt atom were refined. To correct for meaningless distortions, slack soft constraints for bond lengths, bond angles and planarity of the C_6N group were introduced.

Fore the structure determination of (**2**), a slightly different approach was used. Since the Co(2-pmp) groups of (**1**) and (**3**) are practically identical, the entire Co(2-pmp) as determined from (**2**) was defined as rigid body. Thus, a total of nine parameters (3 translations and 3 rotations of the rigid body and 3 positional parameters of the oxygen atom of the free water molecule) were subjected to global optimization. For the final Rietveld refinement, the rigid body was released, using the same soft constraints as for (**3**).

References

Campridge Crystallographic Data Centre, 12 Uunion Road, Cambridge CB2 1EZ, United Kingdom, http://www.ccdc.cam.ac.uk.

Cheary, R. W., Coelho, A. A., Cline,J. P. (2005). J. Res. Natl. Inst. Stand. Technol. 109, 1-25.

Coelho, A.A., J. Appl. Cryst. 33 (2000) 899-908.

Coelho, A.A. J. Appl. Cryst, 36 (2003) 86-95.

Le Bail, A., Duroy, H. & Fourquet, J. L. (1988). Mater. Res. Bull. 23, 447-452.

Rietveld, H. M. (1969). J. Appl. Crystallogr. 2, 65-71.

Stephens, P. W. (1999). J. Appl. Crystallogr. 32, 281-289.)

Computational details.

Table S1. Cartesian coordinates of the hydrated compound **1**.

	x	y	z
Co	0.00000000	-0.00000000	0.00000000
P	3.15646786	0.44923874	0.26339513
O	1.98687395	-0.21694428	-0.48104930
O	4.25237019	-0.56040453	0.54467974
O	3.68413500	1.65464943	-0.50671444
O	-0.17625015	-2.24896703	-0.16164478
H	0.14835147	-2.51177536	-0.95905365
H	0.16242975	-1.98119850	0.33718666
O	-0.45553045	-0.07970982	-2.14516581
H	-1.25333856	-0.23886454	-2.24996911
H	-0.08653940	-0.74154045	-2.41537123
N	0.51047322	-0.29905929	2.08333400
C	-0.29640906	-1.08006106	2.81697197
H	-1.09776111	-1.36425209	2.44034088
C	0.00145793	-1.48328402	4.09888028
H	-0.59440131	-2.00954136	4.58264144
C	1.19968734	-1.09131746	4.64913563
H	1.43256089	-1.35488818	5.51088998
C	2.04772225	-0.30217363	3.90316446

H	2.87013464	-0.04180617	4.25197111
C	1.67273791	0.10129019	2.63002914
C	2.50550539	1.06035374	1.83733392
H	3.25502055	1.33757524	2.38719495
H	1.97108895	1.84960825	1.65779670
O	-1.97835088	-0.09599997	0.46929513
O	0.00692024	2.06248329	0.00674789
P	-3.28097308	-0.26765940	-0.28781182
P	0.53458737	3.26789398	-0.76336168
O	1.70418128	3.93407700	-0.01891724
O	-0.56131496	4.27753724	-1.04464629
H	0.84036280	2.98083603	-1.50268510
H	-1.44995565	4.43088032	-0.74580920
H	5.14101089	-0.71374760	0.24584265
O	-4.10704273	1.02904228	-0.24171644
O	-3.04303152	-0.71807631	-1.72497932
H	-3.82415348	-0.97803383	0.15976298
H	-5.03375387	1.08041164	-0.03906490
H	-3.31912765	-1.36391469	-2.36463838
H	3.40340951	2.27999579	-1.00934267
H	2.26620821	3.38698264	-0.34650464

Table S2. Cartesian coordinates of compound **2**.

	x	y	z
Co	0.00000000	0.00000000	0.00000000
C	1.28092997	-0.34138897	2.79531938
C	-0.85521009	-1.43296380	2.58202901
C	-0.65249069	-1.98919578	3.82956437
N	0.10666365	-0.62772625	2.06349236
C	0.47541888	-1.72505245	4.55839254
C	1.45960080	-0.89554070	4.03710259
C	2.32546722	0.58889432	2.21769519
P	2.97799171	-0.11736889	0.52799518

O	3.96922334	1.02598626	0.01340533
O	3.83859834	-1.35179215	0.83046091
O	1.94023863	-0.30611220	-0.49987159
O	-0.55287765	-1.12762035	-1.67051835
P	1.00816717	3.30000710	-0.50517707
O	0.01698543	2.15676843	0.00933004
O	0.14754795	4.53450684	-0.80776600
O	2.04589931	3.48872470	0.52271555
H	-0.72077500	4.81693057	-0.69528126
H	4.70693628	-1.63417738	0.71799699
O	-2.14695153	0.29147098	0.10072929
H	-1.64852320	-1.60405318	2.08818441
H	-1.30464473	-2.57107648	4.20186788
H	0.58525894	-2.10882162	5.42045790
H	2.24995549	-0.71040355	4.53062435
H	3.13114936	0.45918330	2.70405959
H	2.06978330	1.50325355	2.25044678
H	-0.25745503	-1.78168065	-2.24613116
P	-3.36327048	0.14026049	-0.82335328
H	-1.46832598	-1.20523686	-1.62224793
O	-2.85018072	-0.58488329	-2.15170165
O	-4.08837612	1.35553438	-1.22846462
H	-3.96429872	-0.53901176	-0.42654823
H	-3.23417111	-1.14621566	-2.81499446
H	-5.00935529	1.43480396	-1.00934432
H	1.44708330	2.99079968	-1.16414854
H	2.85575772	3.35621446	0.30119719
H	3.95950613	1.87592572	0.01631929

Table S3. Cartesian coordinates of the dehydrated compound **3**.

	x	y	z
Co	0.00000000	0.00000000	0.00000000
O	3.61034335	-1.98029805	0.55313865

O	-1.58623637	-0.84667628	-0.64658631
P	2.94082969	-0.60730337	0.39856924
C	2.44523911	0.02318077	2.16854917
O	4.08031635	0.42355553	-0.04887424
O	1.85970828	-0.53975788	-0.59981101
N	0.06344982	-0.82991929	1.99188305
O	-0.01087832	1.93218503	0.01838789
C	1.28695596	-0.79270541	2.69985870
C	-0.99647714	-1.52799734	2.47335247
P	1.12860832	2.96304394	-0.42905559
O	2.20972974	2.89549844	0.56932467
H	1.34536411	2.68727903	-1.20331048
O	0.45909466	4.33603861	-0.58362499
C	1.41099309	-1.48390473	3.87824290
C	-0.89467123	-2.21049549	3.64604791
C	0.32487097	-2.20306671	4.36067666
H	-0.17494476	4.91504082	-0.17711490
H	-1.78670264	-1.53809072	2.00235166
H	-1.61720739	-2.67606230	3.97405558
H	0.39853906	-2.67562658	5.14659027
H	2.20687183	-1.46771424	4.33945315
H	4.23016820	-2.53326941	0.15761388
H	3.21124973	-0.26212234	2.59072197
H	2.27249680	0.73764349	2.72181504
P	-2.48583874	-0.96263557	-1.88492956
O	-2.59197790	0.59154363	-2.24997957
O	-3.85673408	-1.48075751	-1.73685984
H	-2.96869292	-2.15573330	-1.70225598
H	-2.65655466	1.51436370	-2.46615762
H	-4.74680552	-1.79981920	-1.64481399
H	4.06641606	1.37334450	-0.03446273
H	2.91373177	2.35131437	0.23654119

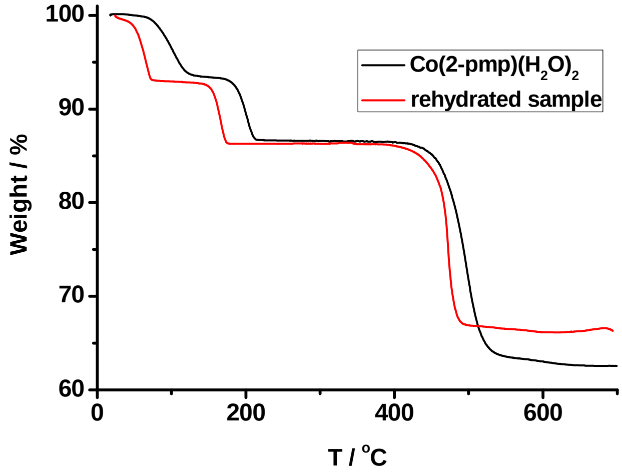
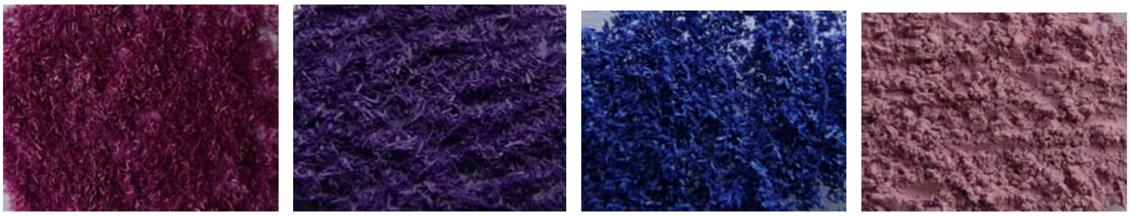


Figure S1. TG curves of compound **1** and **3**-rehydrated.



1 **2** **3** **3**-rehydrated

Figure S2. Color changes of **1** upon heating

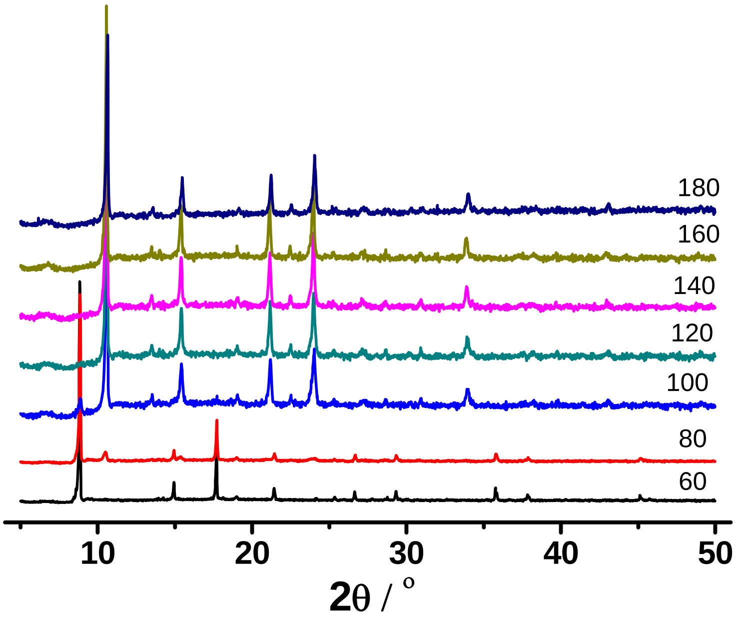


Figure S3. In-situ powder XRD measurement of **1** upon heating. The powder patterns were measured in Bragg-Brentano geometry and exhibit strong preferred orientation.

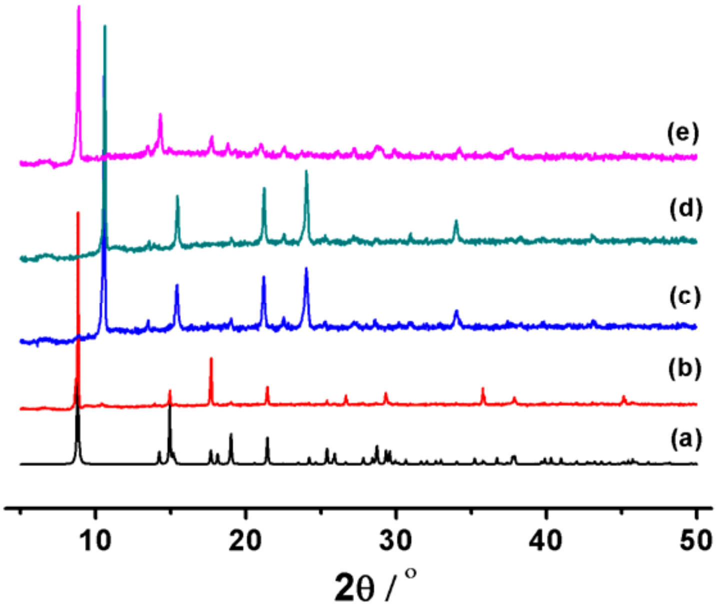


Figure S4 PXRD patterns for compound **1** simulated from single crystal structure (a), compound **1** (b), **2** (c), **3** (d) and **3** after rehydration (e).

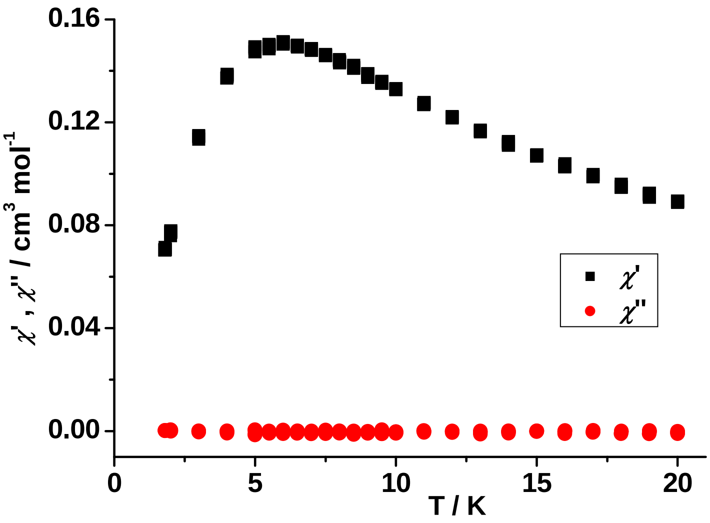


Figure S5 Temperature dependent ac magnetic measurements for compound **1**.

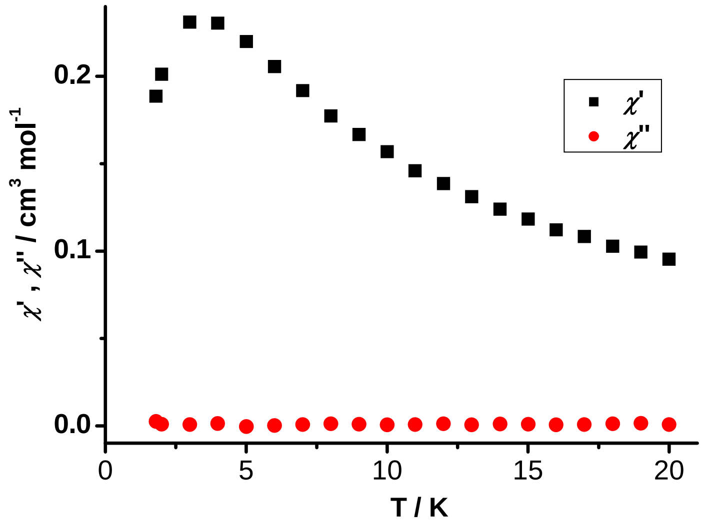


Figure S6 Temperature dependent ac magnetic measurements for compound **2**.

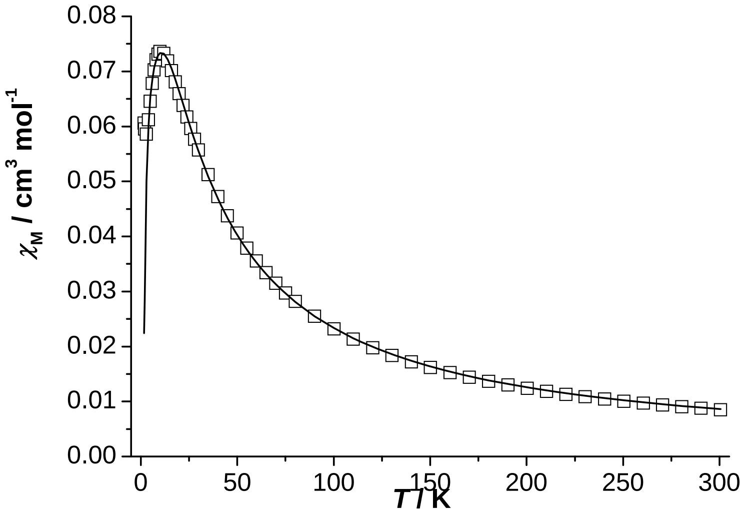


Figure S7 Temperature dependent dc magnetic measurements for compound **3**. Theoretical fitting is shown as the solid line.