Spin Canting in a Unprecedented Three-Dimensional Pyrophosphate- and 2,2'-Bipyrimidine-Bridged Cobalt(II) Framework

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Supporting information

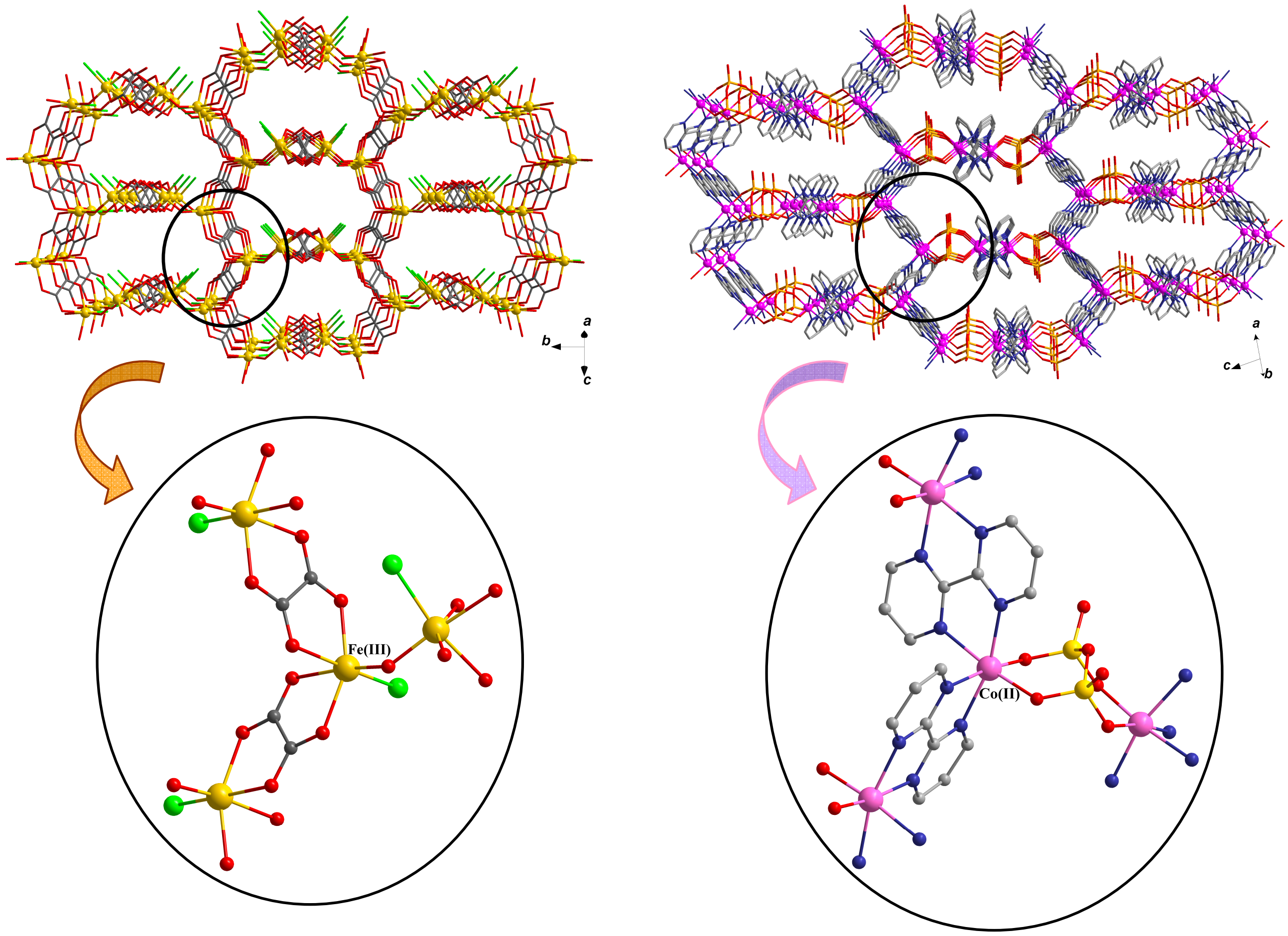

Fig. S1. Comparison between the anionic $[Fe_2(ox)_2Cl_2(\mu\text{-}O)]_n^{2n-}$ open frameworks and compound **1**.

Experimental details for the crystal structure determination of $\{[Co_2(P_2O_7)(bpym)_2] \cdot 12\ H_2O\}_n$ (1).

Single crystal X-ray diffraction data of **1** were collected a T = 100 K on a Bruker-Nonius X8APEXII CCD area detector diffractometer using monochromatized Mo-K_α radiation (λ = 0.71073 Å) and processed through the SAINT[1] reduction and SADABS[2] absorption software. The structure was solved by Patterson method and subsequently completed by Fourier recycling using the SHELXTL[3] software packages and refined by the full-matrix least-squares refinements based on F^2 with all observed reflections.

The crystallization water molecules were located on a ΔF map with some of them disordered on different positions. The right occupancy factors have been defined according to TGA analysis. All non-hydrogen atoms were refined anisotropically, less those of the crystallization water molecules and those of the disordered bpym. The hydrogen atoms of the disordered bpym molecule and of the water molecules were not defined.

Bipyrimidine static disorder in compound 1.

The structural analysis at low temperature reveals that one of the two crystallographic independent bpym molecules in the asymmetric unit of compound **1** is disordered, while the other is well defined. In the refinement of the structure a reasonable model for such a disorder was found identifying two distinct positions for the former molecule (*see* Fig. S1). All attempts to refine anisotropically the atoms of the two sets do not converge to a good model. For this reason they were refined isotropically and no hydrogen atoms were placed in calculated position.

Naming bpym1 and bpym2 the two crystallographic independent bpym molecules, we have:

The **bpym1** molecule is statically disordered into two position (the occupancy factors were refined):

- [N(1)N(2)/N(1b)N(2b)] : ~ 60% (bpym1**A**)
- [N(1A)N(2A)/N(1Ab)N(2Ab)] : ~ 40% (bpym1**B**) [(b) = 2-*x*, 1-*y*, 1-*z*].

The **bpym2** molecule ([N(3)N(4)/N(3c)N(4c)]) is unambiguously defined [(c) = 1.5-*x*, 0.5-*y*, 1-*z*].

Both the bpym1A and bpym1B groups of atoms are almost planar [mean deviation from planarity being 0.0223(3) and 0.0323(3), respectively] and they form a dihedral angle of 17.9(2)°.

The bpym2 molecule is also planar [mean deviation from planarity of 0.0043(2)].

The values of the dihedral angle that the bpym2 molecule forms with the bpym1 disordered one is:

- 78.7(2)°, taking into account bpym2 and bpym1**A**, or
- 88.6(2)°, considering bpym2 and bpym1**B**.

In summary, each cobalt atom is coordinated to:

- the pyrophosphate anion,
- the bpym2 molecule and
- the bpym1**A** (60%) / the bpym1**B** (40%) one.

As a consequence, in the structure of compound **1** every cobalt atoms occupy crystallographically equivalent position, but their chemical (geometrical) environment vary a little, as indicated in Table S1, in a statistic way.

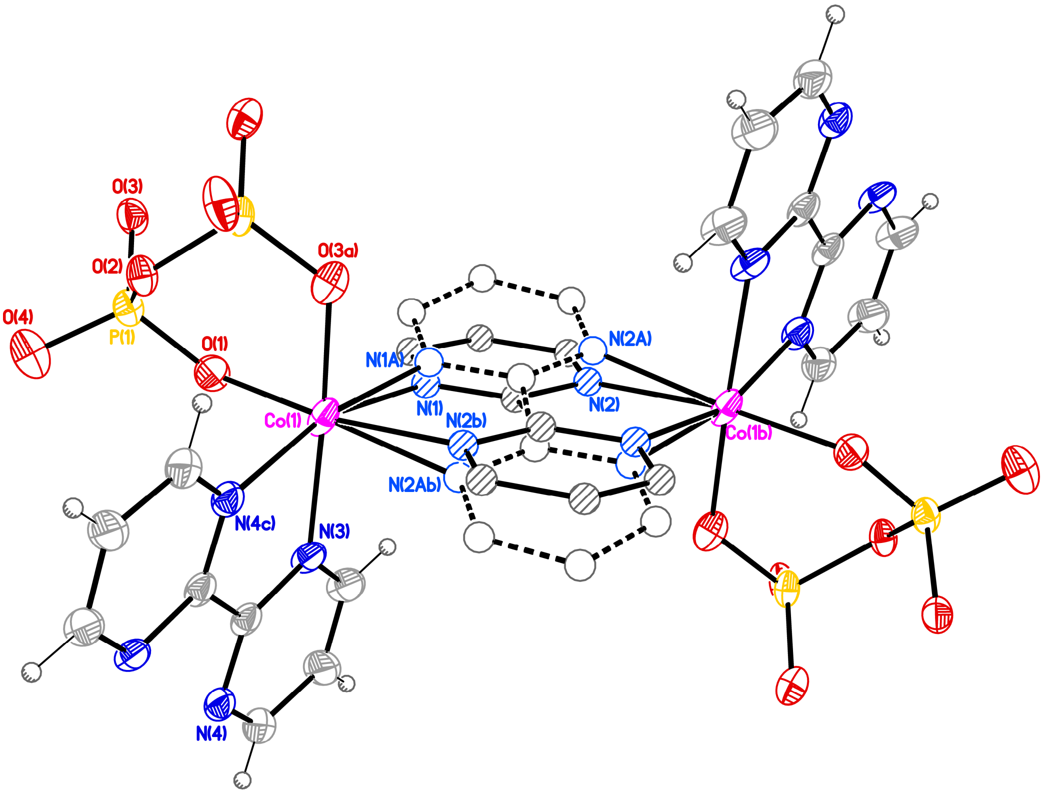

Fig. S2. ORTEP drawing (50% of probability level) of a fragment of the packing of compound **1** showing the environments of two adjacent cobalt ions linked by the bpym1 disordered molecule. Both the [N(1)N(2)/N(1b)N(2b)] (**bpym1A,** shaded circles/full bonds) and the [N(1A)N(2A)/N(1Ab)N(2Ab)] (**bpym1B,** open circles/dashed bonds) sets of atoms have been depicted [symmetry codes: (a) = 2-*x*, *y*, 1.5-*z*; (b) = 2-*x*, 1-*y*, 1-*z* ; (c) = 1.5-*x*, 0.5-*y*, 1-*z*].

Table S1 Cobalt environment in compound **1**, Å/° [in black: unchanging bond lengths/angles; in red: bond lengths/angles in the presence of the bpym1A type molecule; in blue: bond lengths/angles in the presence of the bpym1B type molecule]:

Co(1)-O(1)	2.053(2)	Co(1)-N(3)	2.176(3)
Co(1)-O(3a)	2.042(2)	Co(1)-N(4c)	2.180(3)
Co(1)-N(1)	2.161(5)	Co(1)-N(1A)	2.115(6)
Co(1)-N(2b)	2.194(4)	Co(1)-N(2Ab)	2.142(6)
O(1)-Co(1)-O(3a)	92.5(1)	O(3a)-Co(1)-N(3)	174.7(1)
O(1)-Co(1)-N(3)	88.1(1)	O(3a)-Co(1)-N(4c)	98.8(1)
O(1)-Co(1)-N(4c)	94.5(1)	N(3)-Co(1)-N(4c)	75.9(1)
O(1)-Co(1)-N(1)	92.8(1)	O(1)-Co(1)-N(1A)	95.0(2)
O(1)-Co(1)-N(2b)	170.0(1)	O(1)-Co(1)-N(2Ab)	166.1(2)
O(3a)-Co(1)-N(1)	96.6(2)	O(3a)-Co(1)-N(1A)	86.4(2)
O(3a)-Co(1)-N(2b)	83.0(1)	O(3a)-Co(1)-N(2Ab)	97.1(2)
N(3)-Co(1)-N(1)	88.6(2)	N(3)-Co(1)-N(1A)	98.8(2)
N(3)-Co(1)-N(2b)	97.3(2)	N(3)-Co(1)-N(2Ab)	83.3(2)
N(4c)-Co(1)-N(1)	162.6(2)	N(4c)-Co(1)-N(1A)	169.0(2)
N(4c)-Co(1)-N(2b)	95.0(1)	N(4c)-Co(1)-N(2Ab)	93.9(2)
N(1)-Co(1)-N(2b)	79.0(2)	N(1A)-Co(1)-N(2Ab)	75.7(2)

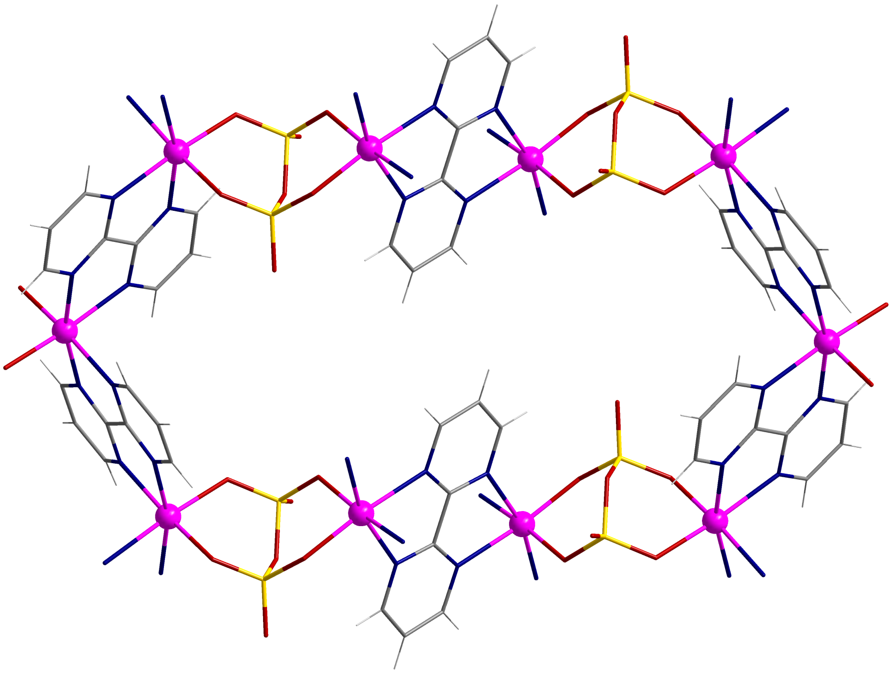

Fig. S3 A view of the pseudo-hexagonal ten-gon ring in **1**.