

# Combination of Organic and Inorganic Cations in Synthesis of Transition Metal Nitrates: Preparation and Characterization of Canted Rectangular Ising Antiferromagnet (PyH)CsCo<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>

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## 1. Synthesis of (PyH)ANi<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (A = Cs, NH<sub>4</sub>)

A mixture containing 0.01 mol of nickel dinitrate hexahydrate Ni(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>, 0.005 mol of pyridinium nitrate PyHNO<sub>3</sub>, and 0.005 mol of cesium nitrate CsNO<sub>3</sub> (or 0.005 mol of ammonium nitrate NH<sub>4</sub>NO<sub>3</sub>) was dissolved in 10 ml of anhydrous HNO<sub>3</sub> under constant stirring. Next, the reaction mixture was placed into a vacuum desiccator over phosphoric anhydride. During the synthesis, the desiccator was repeatedly evacuated, the dryer was updated as necessary. The reaction mixture was kept until the complete removal of the liquid phase. The duration of the synthesis was 2 months. The resulting crystalline sample was characterized by single-crystal X-ray diffraction.

## 2. Structure description

### (a) (PyH)CsCo<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>

Crystal structure of (PyH)CsCo<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (CCDC ref. number 2290111) consists of [Co<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> anions and Cs<sup>+</sup> and PyH<sup>+</sup> cations. Cobalt atoms coordinate six oxygen atoms of one terminal bidentate and four bridging monodentate nitrate groups (two syn-anti and two anti-anti types) at distances of 2.079(3) – 2.173(3) Å forming quite symmetrical octahedron. The cobalt ions in the [Co<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> anionic layer are transformed by means of *m* plane along *b*-axis and *a* glide plane along *c*-axis. The latter lead to the corrugation of the layer – deviation of cobalt ion along *a*-axis with the Co...Co...Co angle equal to 124.9°. The Co...Co separation in layer vary in the range of 4.901(1) Å (along *a*) and 5.957(1) Å (along *b*). The anionic layers are interlinked by cationic layers composed by Cs<sup>+</sup> and pyridinium PyH<sup>+</sup>. The Cs<sup>+</sup> forms ten shortened contacts (3.007(1)-3.582(1) Å) with nitrate groups, while pyridinium cations are involved in the weak N-H...O hydrogen bond with N...O equal to 3.008(6) Å. Thus, crystal structure of [Co<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> can be described as the layered one with Co...Co separation between two anionic layers equal to 7.812(1) Å.

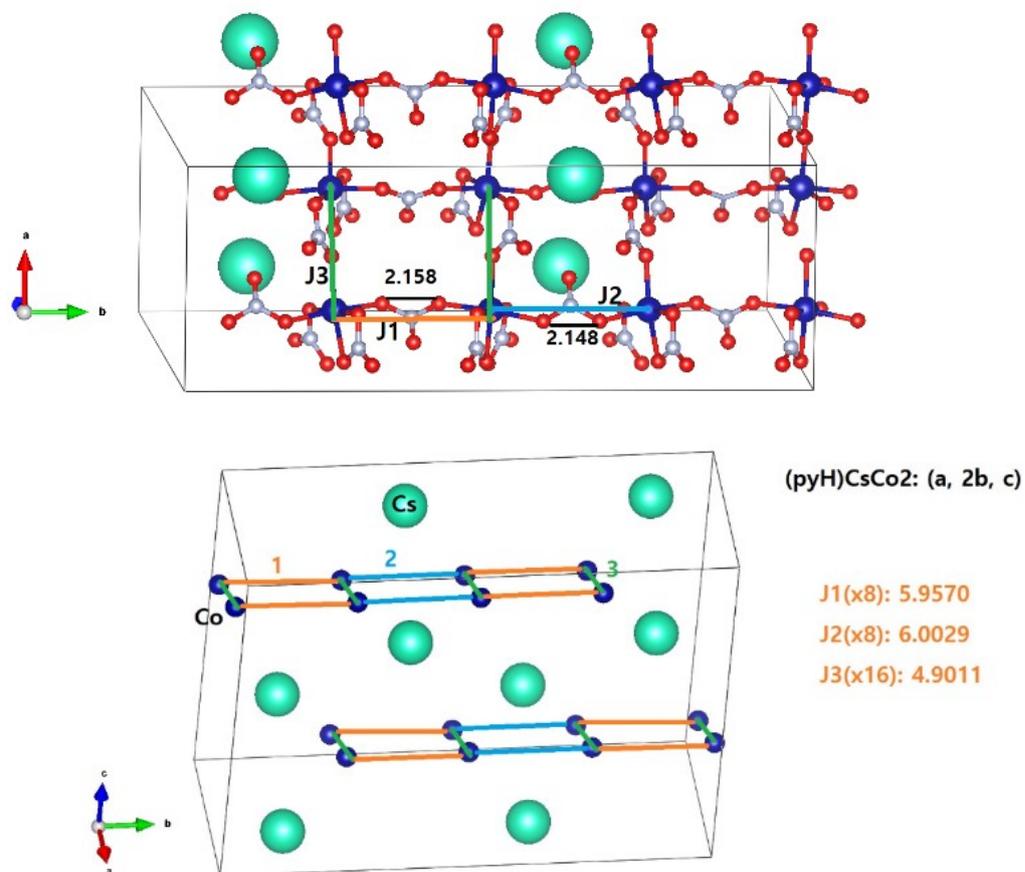
The structure of [Co<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> layers resembles that in the structure of Co(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> [1]. However, in the structure of cobalt dinitrate dihydrate, the rectangular layers are almost planar due to a different type of bridging nitrate groups linking the metal atoms (only anti-anti type), which increases the distance between the metal atoms inside such a layer (the smallest Co – Co distance is 5.92 Å). In case of Co(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> the layers are linked to each other by hydrogen bonds between axially coordinated water molecules are located at a distance of 4.25 Å relative to each other.

### (b) (PyH)ANi<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (A = Cs, NH<sub>4</sub>)

These nickel compounds are isostructural to the cobalt one. Crystal structure of PyHCsNi<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (CCDC ref. number 2291442) and PyHNH<sub>4</sub>Ni<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (CCDC ref. number 2291443) consists of anionic layers [Ni<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup> and Cs<sup>+</sup> (or NH<sub>4</sub><sup>+</sup>) and PyH<sup>+</sup> cations. The Ni...Ni separations between the layered anions are equal to 7.717(2) Å and 7.560(2) Å for (PyH)CsNi<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> and (PyH)NH<sub>4</sub>Ni<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> respectively which is due to the smaller size of ammonium cation than that of cesium.

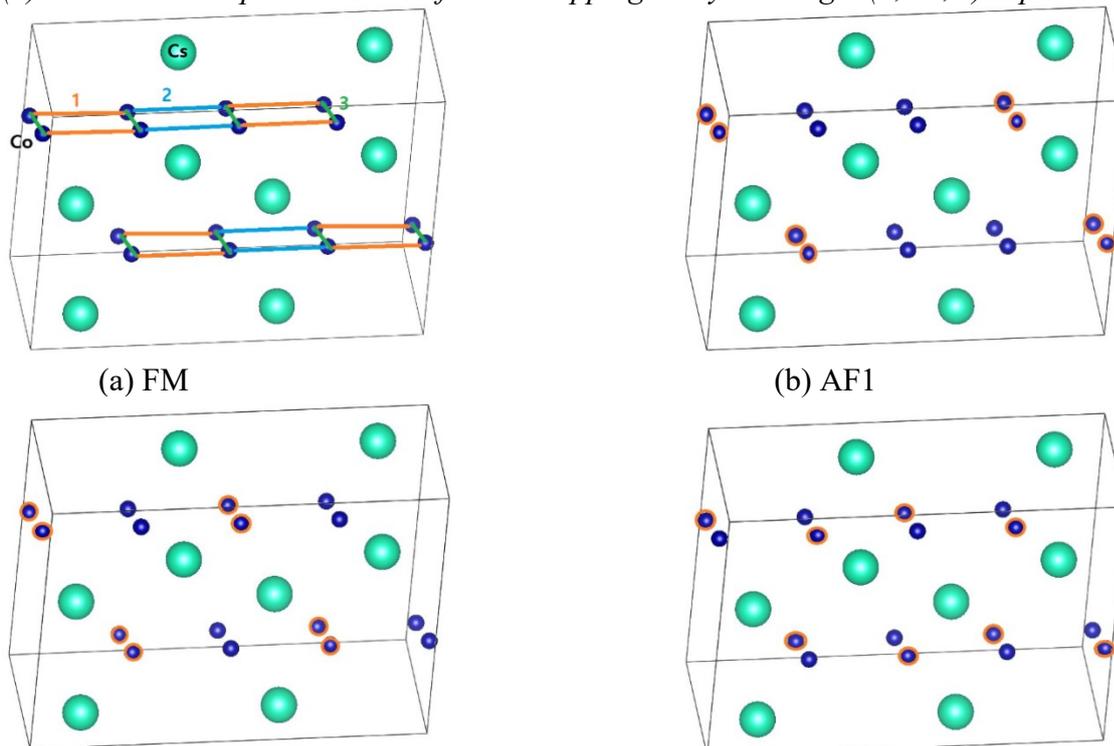
### 3. Evaluation of the spin exchanges $J_1$ , $J_2$ and $J_3$ by energy-mapping analysis based on DFT calculations

(a) Spin exchange paths



**Fig. S1.** Spin exchange paths  $J_1$ ,  $J_2$  and  $J_3$  in (PyH)CsCo<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>.

(b) Four ordered spin states used for the mapping analysis using a (a, 2b, c) supercell



(c) AF2

(d) AF3

**Fig. S2.** Spin arrangements of the ordered spin states FM, AF1, AF2, and AF3 state. The orange and blue circles indicate up-spin and down-spin  $\text{Co}^{2+}$  ion sites, respectively.

(c) Energies of the ordered spin states in terms of the spin exchanges

$$E_{\text{FM}} = (-8J_1 - 8J_2 - 16J_3)S^2$$

$$E_{\text{AF1}} = (+8J_1 - 8J_2 - 16J_3)S^2$$

$$E_{\text{AF2}} = (+8J_1 + 8J_2 - 16J_3)S^2$$

$$E_{\text{AF3}} = (+8J_1 + 8J_2 + 16J_3)S^2$$

(d) Spin exchanges in terms of the energies of ordered spin states

$$J_1 = (E_{\text{AF1}} - E_{\text{FM}})/(16S^2)$$

$$J_2 = (E_{\text{AF2}} - E_{\text{AF1}})/(16S^2)$$

$$J_3 = (E_{\text{AF3}} - E_{\text{AF2}})/(32S^2)$$

(e) Relative energies of the ordered spin states in terms of DFT+U calculations

Computational parameters

Exchange-correlation functional = PBE

Threshold for SCF convergence =  $10^{-6}$  eV

Kpoint = (8x2x4)

Plane wave cut-off energy = 450 eV

Table 1. Relative energies (in meV/FUs) obtained from DFT+U calculations

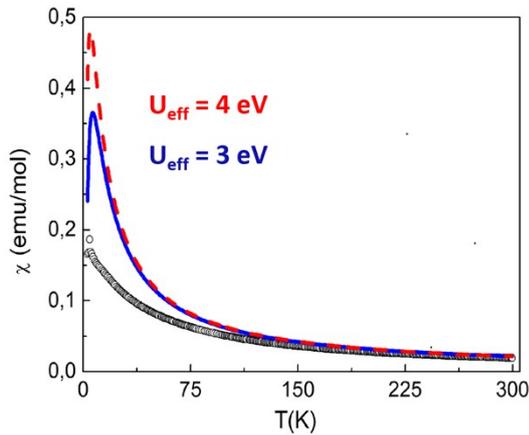
|     | $U_{\text{eff}} = 3$ eV | $U_{\text{eff}} = 4$ eV |
|-----|-------------------------|-------------------------|
| FM  | 10.99                   | 8.32                    |
| AF1 | 6.17                    | 4.74                    |
| AF2 | 0.74                    | 0.59                    |
| AF3 | 0                       | 0                       |

(f) Values of the spin exchanges

Table 2. Spin exchange parameters (in K) obtained from DFT+U calculations

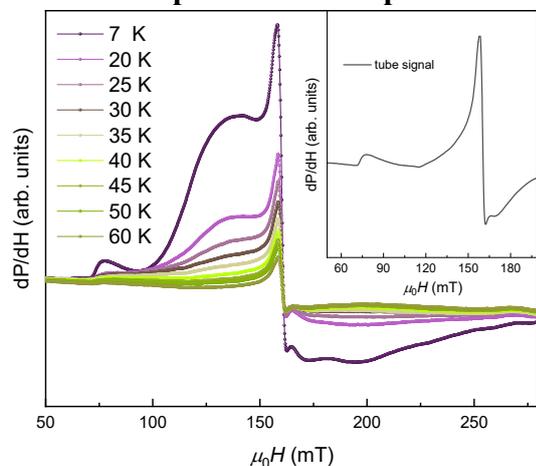
|       | $U_{\text{eff}} = 3$ eV | $U_{\text{eff}} = 4$ eV |
|-------|-------------------------|-------------------------|
| $J_1$ | -12.41                  | -9.25                   |
| $J_2$ | -14.02                  | -10.70                  |
| $J_3$ | -0.95                   | -0.76                   |

#### 4. Fitting of the temperature dependence of magnetic susceptibility



**Fig. S3.** Temperature dependence of the magnetic susceptibility  $\chi$  measured for a crystalline powder sample of  $(\text{PyH})\text{CsCo}_2(\text{NO}_3)_6$  taken at  $\mu_0 H = 0.1$  T (symbols) and fits by Eq. 3 for  $U_{\text{eff}} = 3$  eV (blue solid line) and  $U_{\text{eff}} = 4$  eV (red dashed line).

## 5. Electron spin resonance spectra



**Fig. S4.** The temperature evolution of the ESR spectra measured for  $(\text{PyH})\text{CsCo}_2(\text{NO}_3)_6$ . The inset represents the signal taken from the measurement tube at  $T = 7$  K.

[1] Wildner M, Giester G, Lengauer Ch L and Zemmann J 2012 Investigation of low-hydrated metal (II) nitrates. Syntheses and crystal structures of  $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{M}(\text{II})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}$ ). *Z. Krist.* **227**, 129–140