Supplementary Materials to

A Missing Nuclearity in the Co(III)/Ln(III)/2-pyridyladoxime Chemistry: Tetranuclear Compounds Using the "Assisted Self-Assembly" Approach (Ln= Rare Earth Metals)

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S1 PXRD Measurements

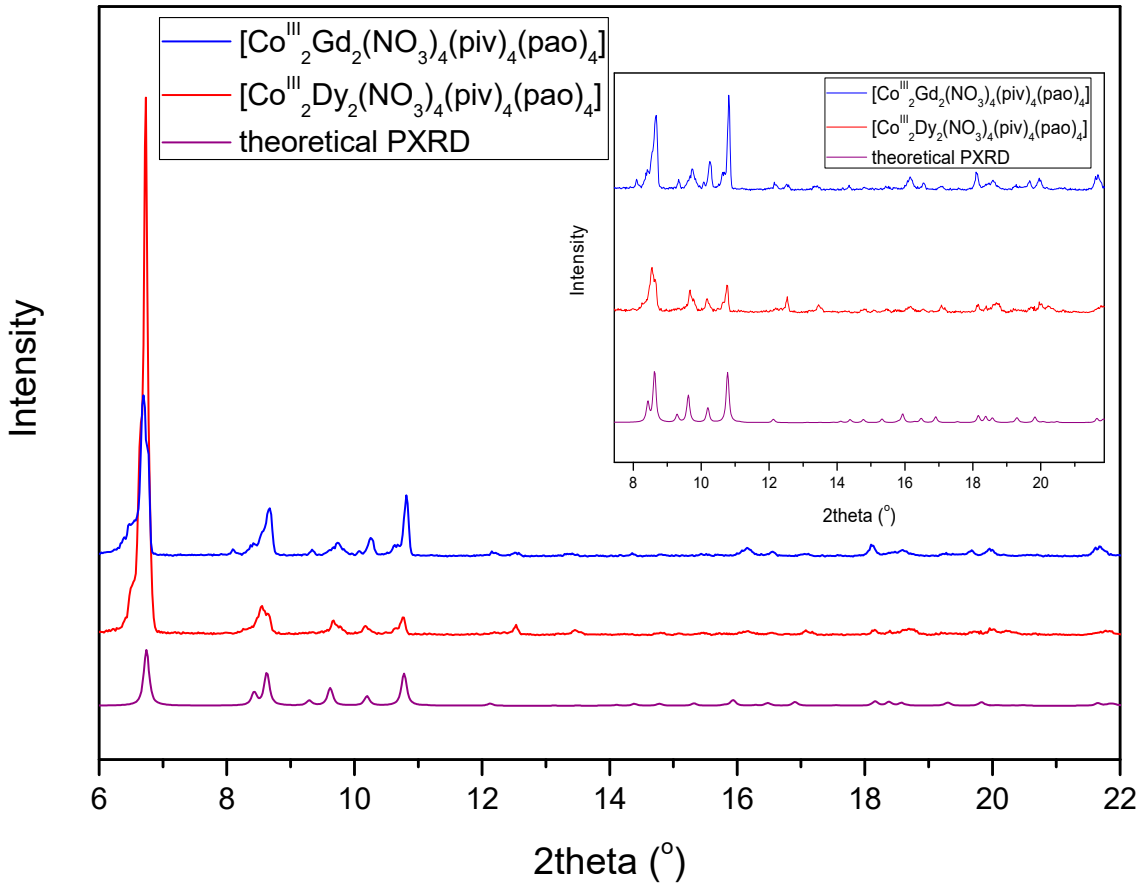

Figure S1. Comparison of the theoretical PXRD diagram of **1**·2MeCN with the experimental ones for **1** and **2.**

S2 Infrared (FT-IR) Spectroscopic Characterization

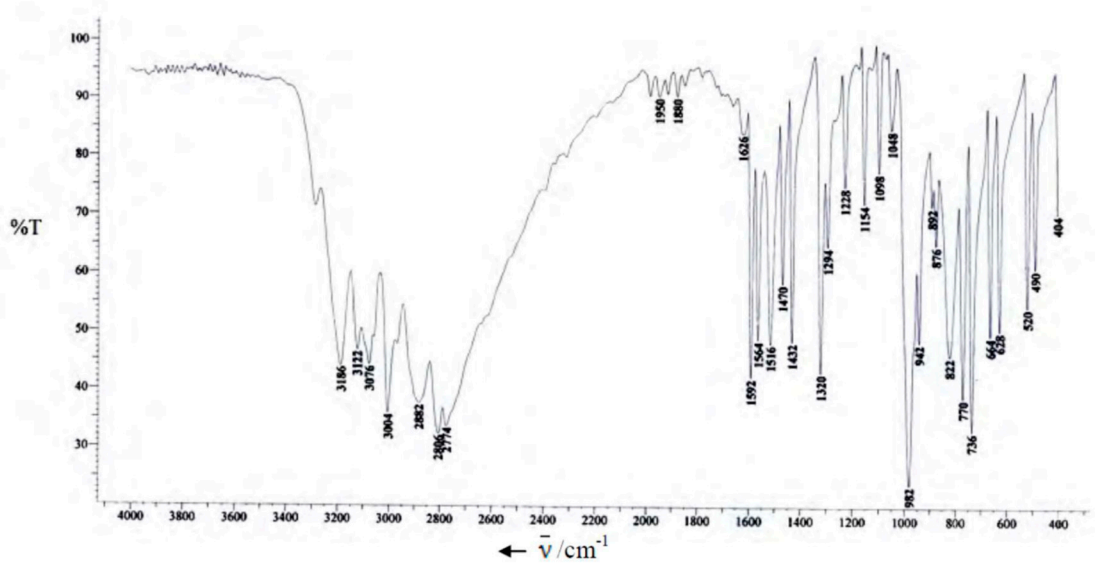

Figure S2. The FT-IR spectrum (KBr/cm^{-1}) of free paoH.

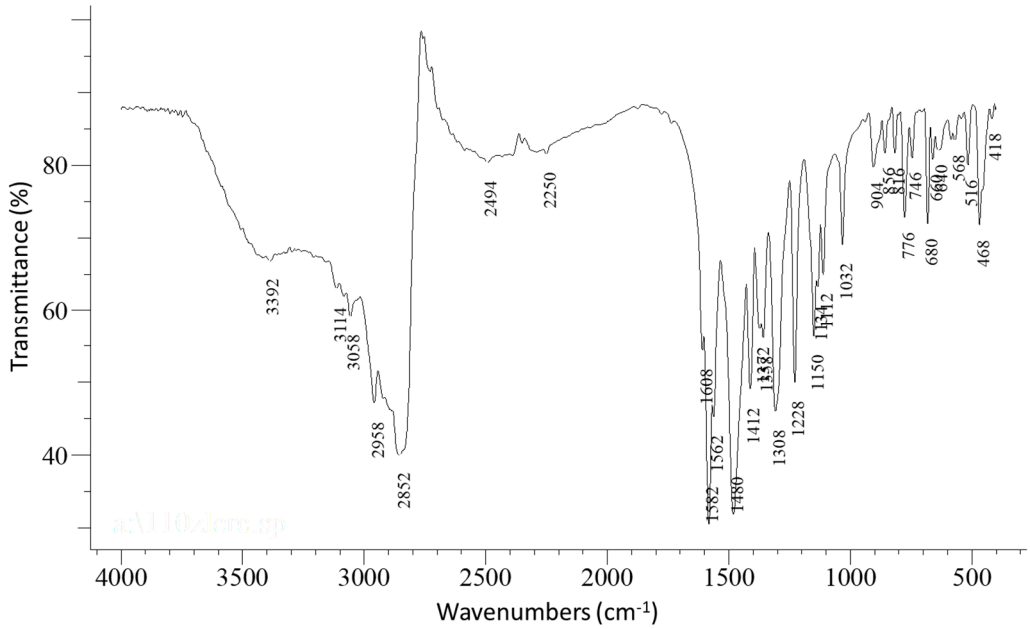

Figure S3. The FT-IR spectrum (KBr, cm^{-1}) of a well-dried (i.e., without lattice MeCN) sample of $[Co^{III}_2Pr_2(NO_3)_4(piv)_4(pao)_4]$ (**4**).

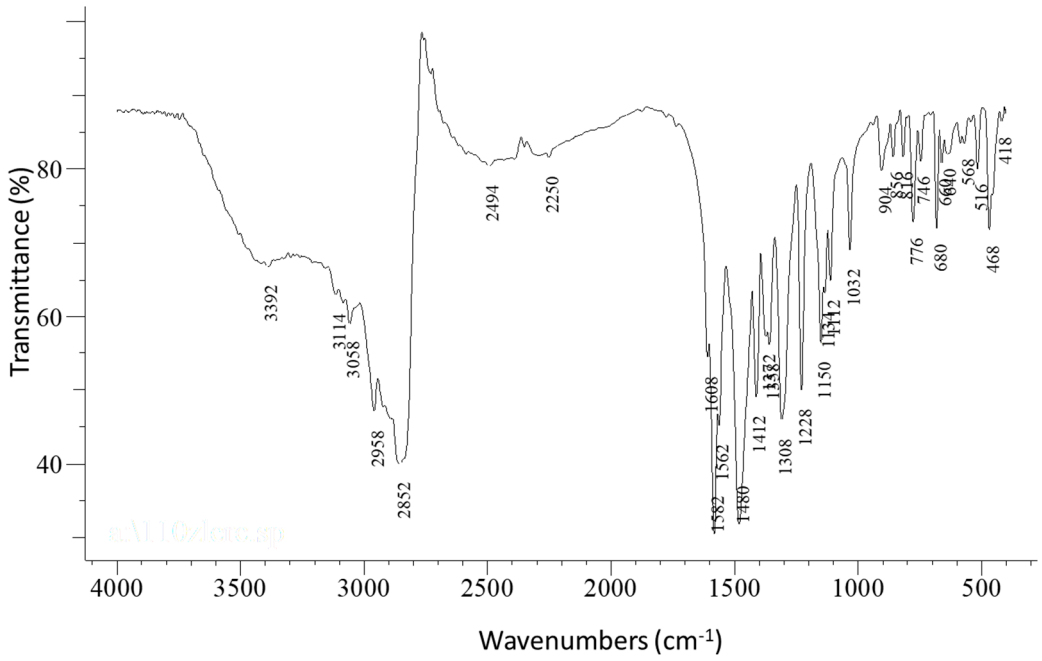

Figure S4. The FT-IR spectrum (KBr, cm^{-1}) of a well-dried (i.e., without lattice MeCN) sample of $[Co^{III}_2Gd_2(NO_3)_4(piv)_4(pao)_4]$ (**2**).

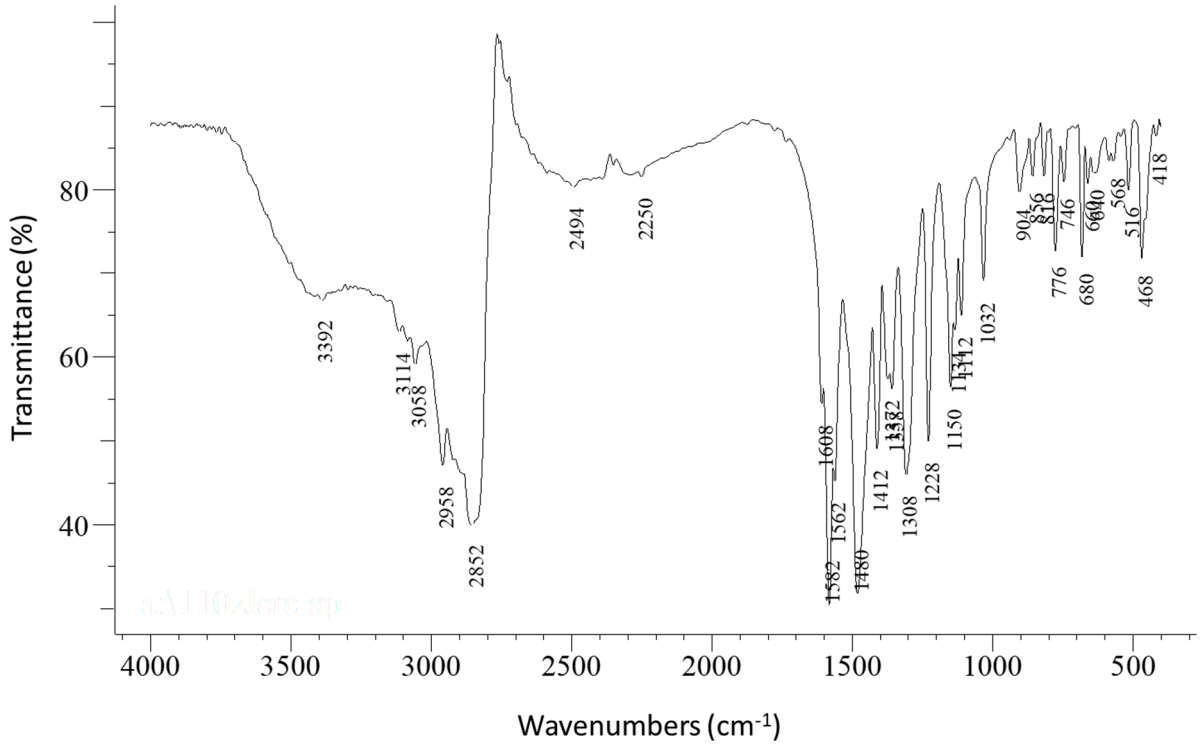

Figure S5. The FT-IR spectrum (KBr, cm^{-1}) of a well-dried (i.e., without lattice MeCN) sample of $[Co^{III}_2Tb_2(NO_3)_4(piv)_4(pao)_4]$ (**3**).

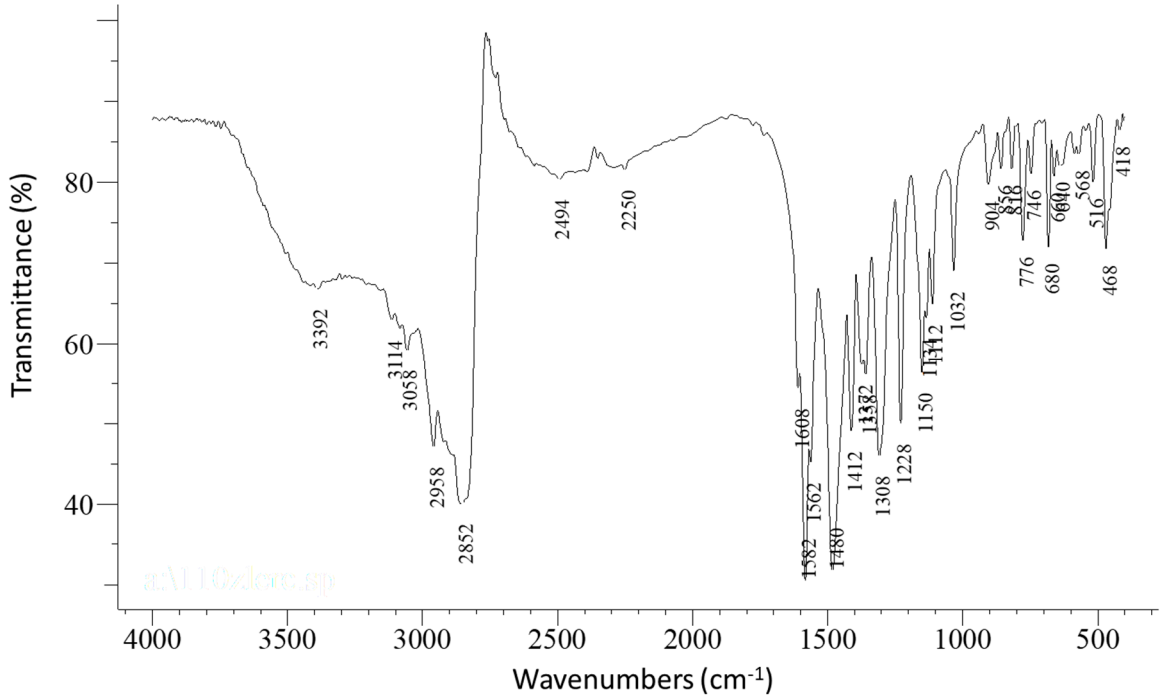

Figure S6. The FT-IR spectrum (KBr, cm^{-1}) of a well-dried (i.e., without lattice MeCN) sample of $[Co^{III}_2Y_2(NO_3)_4(piv)_4(pao)_4]$ (**5**).

S3 Crystal Lattice Interactions

Table S1. Intra- and intermolecular interactions in the crystal structure of **1**·2MeCN.

Interaction	D···A (Å)	H···A (Å)	D-H···A (°)
	intramolecular		
C(6)-H(6)···N(4)	3.019	2.534	111.9
	intermolecular		
C(6)-H(6)···N(4)	3.019	2.534	111.9
C(12)-H(12)···O(5)	2.962	2.462	112.8
	with the MeCN solvents		
C(2S)-H(2S1)···O(9)	3.522	2.587	159.7
C(2S)-H(2S2)···O(11)	3.413	2.580	142.9