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Effects of Anion and Bipyridyl Bridging Ligand Identity on the Co(II) Coordination Networks

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Abstract

Five new coordination polymers, $\{[\text{Co}(\text{OAc})_2(\text{bpe})(\text{H}_2\text{O})] \cdot 0.5(\text{dmf})\}_n$ (1), $\{[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4][\text{Co}(\text{tfa})(\text{bpy})_2(\text{H}_2\text{O})_3](\text{tfa})_3 \cdot 1.5(\text{bpy})\}_n$ (2), $[\text{Co}(\text{tfa})_2(\text{dps})_4]_n$ (3), $\{[\text{Co}(\text{tfa})_2(\text{bpe})_4] \cdot \text{H}_2\text{O}\}_n$ (4), and $[\text{Co}(\text{tfa})_2(\text{bpp})_4]_n$ (5) (where $\text{AcO}^- = \text{CH}_3\text{CO}_2^-$; $\text{tfa}^- = \text{CF}_3\text{CO}_2^-$; $\text{bpy} = 4,4'$ -bipyridine; $\text{bpe} = 1,2$ -bis(4-pyridyl)ethane; $\text{bpp} = 1,3$ -bis(4-pyridyl)propane; $\text{dps} = 4,4'$ -dipyridyl sulfide; $\text{dmf} = \text{N,N}'$ -dimethylformamide) were synthesized by the reactions of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{tfa})_2 \cdot 4\text{H}_2\text{O}$ with different dipyridyl ligands and characterized by elemental analysis, IR spectra, and X-ray single-crystal diffraction. Compound 1 exhibits extended two-dimensional (2D) networks through the bridging AcO^- and bpe ligands. The polymeric motifs in 2–5 are exclusively based on bipyridine-type ligands and results in 1D cationic chains in 2, similar charge-neutral double tapes in 3 and 4, and a 2D polymeric network in 5. In 2–5, the tfa anions coordinate to the Co(II) center in a monodentate mode. An impact of the anion's fluorination on coordination modes and supramolecular architectures is registered. Magnetic measurements reveal almost vanishing exchange interactions in the layered



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materials 1 and 5. The correlation of mechanical properties and crystal structure has been demonstrated for 1.