

PREPARATION, STRUCTURE AND SELECTED PROPERTIES OF NEW Co(II) CRYSTALLINE SOLIDS

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Nowadays the Co(II)-based coordination networks function as effective heterogeneous and reusable catalysts [1], are discussed as prototypes of future magnetic materials [2] and effective biodegradable drug carriers [3]. Solvatochromism as the inherent property allows using them as sensors for small molecules showing guest selectivity and providing a response in the UV/Vis/NIR spectral range to the guest inclusion [4].

Five new coordination polymers, $\{[\text{Co}(\text{OAc})_2(\text{bpe})(\text{H}_2\text{O})] \cdot 0.5(\text{dmf})\}_n$ (**1**), $\{[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4][\text{Co}(\text{Tfa})(\text{bpy})_2(\text{H}_2\text{O})_3](\text{Tfa})_3 \cdot (\text{bpy})_{1.5}\}_n$ (**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; $\text{dmf} = N,N'$ -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 dipyriddy ligands and characterized by elemental analysis, IR spectra, and X-ray single-crystal diffraction. The IR spectra of complexes **1–5** exhibit very strong and broad bands due to asymmetric and symmetric stretching of coordinated carboxylic groups in the 1609–1564 ($\nu_{\text{as}}\text{COO}$) and 1458–1411 cm^{-1} ($\nu_{\text{s}}\text{COO}$) regions for acetate anion in **1**, and in the 1703–1589 and 1465–1415 cm^{-1} regions for trifluoroacetates in **2–5**, respectively. These bands overlap with the $\nu(\text{C}=\text{N})$ stretching vibrations of the aromatic rings of the pyridyl containing ligands. The IR spectra of **2–5** also display strong bands in the range 1203–1125 cm^{-1} arising from $\delta(\text{C}-\text{F})$ asymmetric and symmetric bending vibrations of Tfa^- groups. The presence of the coordinated water molecules in **1** and **2** is justified by broad signals at 3265 and 3229 cm^{-1} , respectively. The single crystal X-ray analysis revealed the 2D polymeric networks in **1** and **5**, 1D cationic chains in **2**, and similar charge-neutral double tapes in **3** and **4**. An impact of the anion's fluorination on coordination modes and supramolecular architectures is registered and discussed. Magnetic measurements for the two layered structures **1** and **5** indicate that the Co(II) centers interact only very weakly. The mechanical properties for **1** reveal pronounced anisotropy of hardness with the most soft layer facet.

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References

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