Selective Synthesis of Cobalt Oxo Cubane Polymorphs

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More than 100 years after Alfred Werner laid the foundations of modern coordination chemistry, the predictive synthesis and mechanistic understanding of multinuclear clusters remain limited.[1] This work focuses on transition metal oxo cubanes, which are of particular interest due to their potential applications as single-molecule magnets,[2] water-oxidation catalysts,[1] and their structural similarity to the oxygen-evolving complex (OEC) in photosystem II (PSII).[1]

These clusters can be formed with di(2-pyridyl) ketone as a ligand under ambient conditions.[1] The ligand exhibits a variety of versatile binding modes, providing exceptional coordinative flexibility.[2] As a result, three distinct cubane polymorphs can be obtained, each displaying different structural features while maintaining the cuboidal $\{Co_4O_4\}$-core.[1,2] Differentiation between these polymorphs can be readily achieved using powder and single-crystal X-ray diffraction. These structural variations lead to differences in chemical properties, as certain structural features are known to enhance water-oxidation activity.[1]

We present insights into the selective synthesis of these cobalt oxo cubane types, moving toward a more predictive approach to their formation.[3] Convenient parameter changes of the reaction conditions, particularly the choice of counterions[1,4] and solvents, strongly direct the resulting cubane structure. The obtained polymorphs were first detected in solution by ^{1}H NMR spectroscopy to investigate their transformation processes and their presence was subsequently confirmed in the solid state by powder and single-crystal X-ray diffraction analyses of isolated solid products.[3]

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