

From oxido-bridged dimers to hydrogen-bonded assemblies: steric control of self-assembly in *cis*-dioxovanadium(v) Schiff-base complexes

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Streszczenie

cis-Dioxidovanadium(v) (*cis*-VO₂⁺) moieties are among the most fundamental structural units in vanadium(v) coordination chemistry, yet the factors governing their nuclearity, self-assembly, and crystallization remain poorly understood. Here, we investigate these factors in a family of *cis*-VO₂⁺ Schiff-base complexes derived from HSHED, the monoanionic coordinating form of *N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine, which has recently been identified as a precursor to complexes with potential activity against glioblastoma. The coordination environments were characterized in the solid state by single-crystal X-ray diffraction, in solution by multinuclear NMR and UV–visible spectroscopy, and by density functional theory calculations. Previously reported members of this family crystallize exclusively as oxido-bridged dinuclear complexes containing the characteristic covalent O–V–O–V diamond core. To investigate the factors controlling this aggregation, sterically modified ligands were designed to inhibit oxido-bridge formation. New crystal structures presented here include the oxido-bridged dimer [VO₂(3-OEt-5-Ad-HSHED)]₂ together with two members of this family with sterically hindered Schiff base scaffolds forming systems that undergo different self-assembly processes forming a tetramer, [VO₂(3-*t*-Bu-HSHED)]₄ and dimer, [VO₂(3,5-di-*t*-Bu-HSHED)]₂. The [VO₂(3-*t*-Bu-HSHED)]₄ crystallizes as a H-bonded tetranuclear assembly comprising four crystallographically independent mononuclear complexes. The assembly incorporates four distinct ligand–metal stereoisomers arising from both ligand centered stereochemistry and metal coordination chemistry differences while preserving the characteristic *cis*-VO₂⁺ coordination environment at each vanadium center. Rather than exhibiting strong stereochemical discrimination during crystallization, the assembly accommodates multiple stereochemical variants within a common H-bonding network. Complementary solution

studies using ^{51}V and ^1H NMR and UV-vis spectroscopy demonstrate that all the complexes form mononuclear species in solution. Collectively, these results show that self-assembly in this family is governed by a hierarchy of structural factors in which the preferred local coordination geometry of the *cis*- VO_2^+ unit is strongly conserved and steric effects redirect aggregation from covalent O–V–O–V diamond core formation to H-bonded supramolecular assembly. The crystal structure demonstrates that multiple stereoisomers are incorporated within the same H-bonded assembly, suggesting that the coordination preferences of the *cis*- VO_2^+ unit together with the H-bonding network outweigh stereochemical discrimination during crystallization.

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