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A decavanadate containing copper(II) cyclen-complexes: synthesis, theoretical calculations and methylene blue adsorption studies

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Decavanadate, $[H_xV_{10}O_{28}]^{(6-x)-}$, V_{10}, has been widely used as a building block for creating complex supramolecular structures [1]. A novel metal-organic hybrid decavanadate decorated with a copper(II) complex of the macrocycle cyclen (1,4,7,10-tetraazacyclododecane) was synthesized and characterized by diffractometric and spectroscopic techniques. Single-crystal X-ray diffraction analysis revealed that, in the molecular structure of $[\{Cu(cyclen)\}_2(V_{10}O_{28})]\cdot 6H_2O$ (**Cu-cyclen-V_{10}**), the two $[\{Cu_2(cyclen)_2\}^{2+}$ moieties are bound to V_{10} through μ_3-O atoms (Figure below). To the best of our knowledge, it is a new coordination mode of Cu^{II}-V_{10}, which was studied through computational methods, such as Density Functional Theory (DFT) at the B3LYP/LANL2DZ level, Non-Covalent Interaction (NCI), and Independent Gradient Model (IGM). The low Intrinsic Bond Strength Index value of 0.105 indicates a weak Cu–μ_3-O(V_{10}) covalent interaction, *ca.* 2/3 of a usual coordination bond. Moreover, the NCI analysis revealed that **Cu-cyclen-V_{10}** exhibits strong intermolecular interactions between V_{10} and the copper(II) complex, evidencing that non-covalent interactions play a key role in stabilizing the particular conformation presented by the metal-organic aggregate. **Cu-cyclen-V_{10}** was active in bleaching a methylene blue (MB) aqueous solution at 10 mg L^{-1}, achieving 84% of color removal in only 40 min. Physisorption studies with $N_{2(g)}$ gave a type II adsorption isotherm, a calculated BET-specific surface area of 6 $m^2\ g^{-1}$, and a measured total pore volume of 0.01 $cm^3\ g^{-1}$, supporting the compound's fundamentally nonporous nature. Our findings suggest that MB adsorption most likely takes place on the external surface of the **Cu-cyclen-V_{10}** particles.

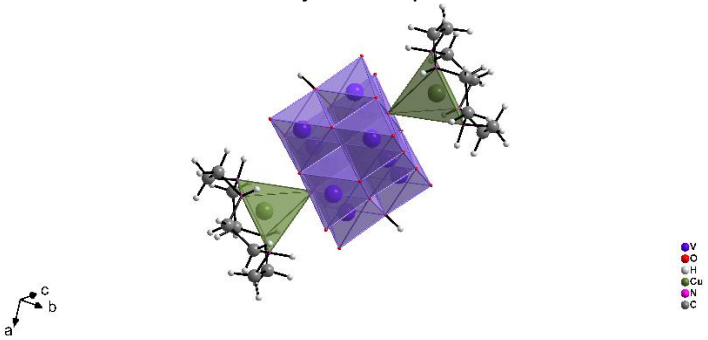

Figure 1. Polyhedral representation of **Cu-cyclen-V_{10}**.

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References

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