



Novel vanadium-peroxido-bis(2-pyridylcarbonyl)amine compounds as hydrocarbon catalysts



LABORATORY OF INORGANIC CHEMISTRY
AND ADVANCED MATERIALS

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Abstract: The synthesis of metal-organic complexes was studied in our Laboratory, with V(V) selected as the transition metal component. The choice of this metal ion was made based on its noteworthy properties, including various oxidation states that render it ideal for redox reactions, the ability to form stable polyoxovanadates (POVs) and metal-organic complexes, as well as the flexibility to achieve diverse coordination geometries upon substrate binding. 2-Picolylamine was chosen as a bidentate ligand, since it contains two donor sites: the pyridine nitrogen and the amine nitrogen, both capable of coordinating to the metal center. Metal coordination leads to the formation of stable chelate rings and enhancement of the metal's catalytic activity. New mononuclear peroxido species, emerging through synthesis, were isolated in crystalline form and characterized through an array of modern physicochemical techniques.

Introduction



Fig. 1: Vanadium(V) oxide (V₂O₅)

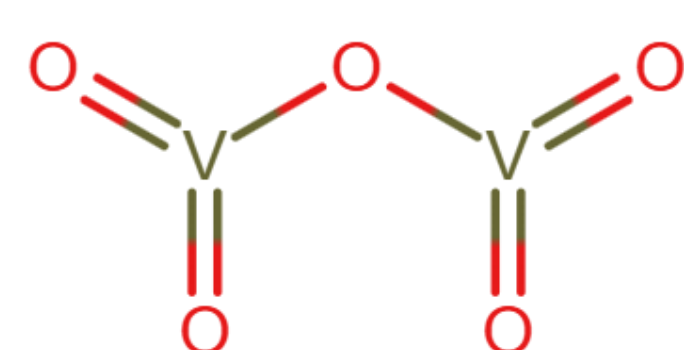
Vanadium is an early first-row transition metal, which is abundant in nature, in minerals, and fossil fuel deposits. Applications of vanadium compounds span a wide array of fields, including pharmaceutical chemistry, industrial catalysis and biocatalysis, nanotechnology, and various biochemical processes.^{1,2} Known for their catalytic activity, primarily due to vanadium's ability to adopt multiple oxidation states, vanadium compounds (Fig. 1) are employed as catalysts in industrial processes. A prominent application is sulfuric acid production via the Contact Process, where V₂O₅ catalyzes the oxidation of SO₂ to SO₃. Additional examples include the: (i) oxidation of alcohols to carbonyl compounds (aldehydes or ketones), using hydrogen peroxide as the oxidizing agent, (ii) selective epoxidation of olefins or oxidation of alkenes to epoxides (for pharmaceutical or fine chemical synthesis), and (iii) polymerization of diolefins (in the production of synthetic rubber). Due to the positive outcomes of research in recent years, significant efforts are being directed toward the synthesis of new vanadium-based compounds in order to enhance the yield of industrial processes of new organic product manufacturing.³⁻⁵

Materials and methods

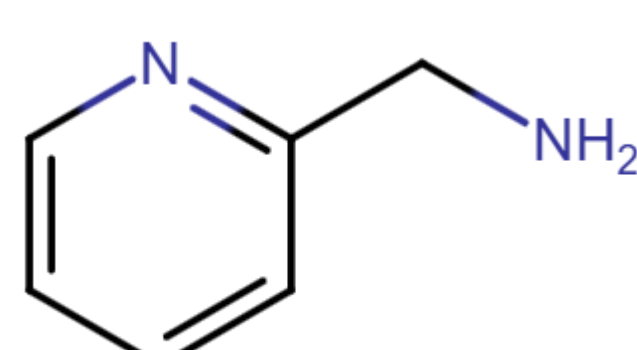
Materials: V₂O₅, 2-picolylamine, hydrogen peroxide, ethanol

Synthesis: Reaction in aqueous media at low temperature

Physicochemical Characterization: elemental analysis, Fourier Transform Infrared Spectroscopy (FT-IR), Raman, NMR, UV-Visible, cyclic voltammetry, thermogravimetric analysis (TGA-DTG), X-ray crystallography



V₂O₅



2-Picolylamine

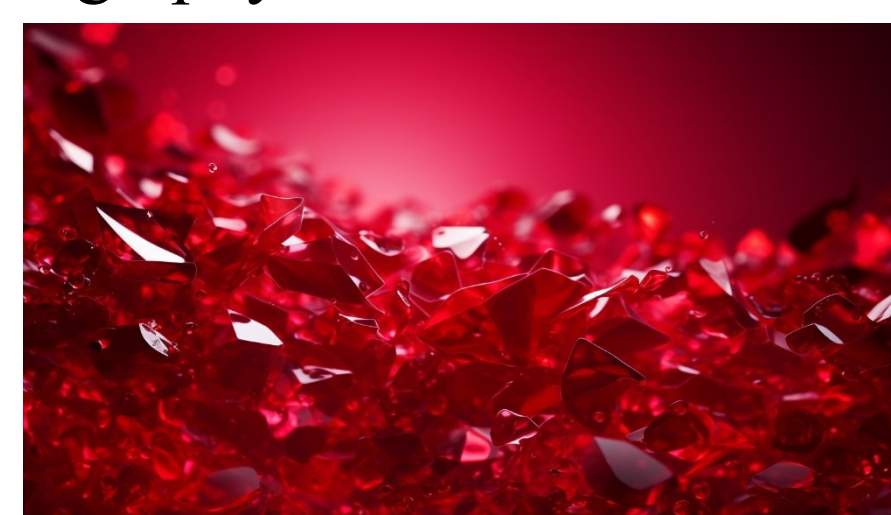
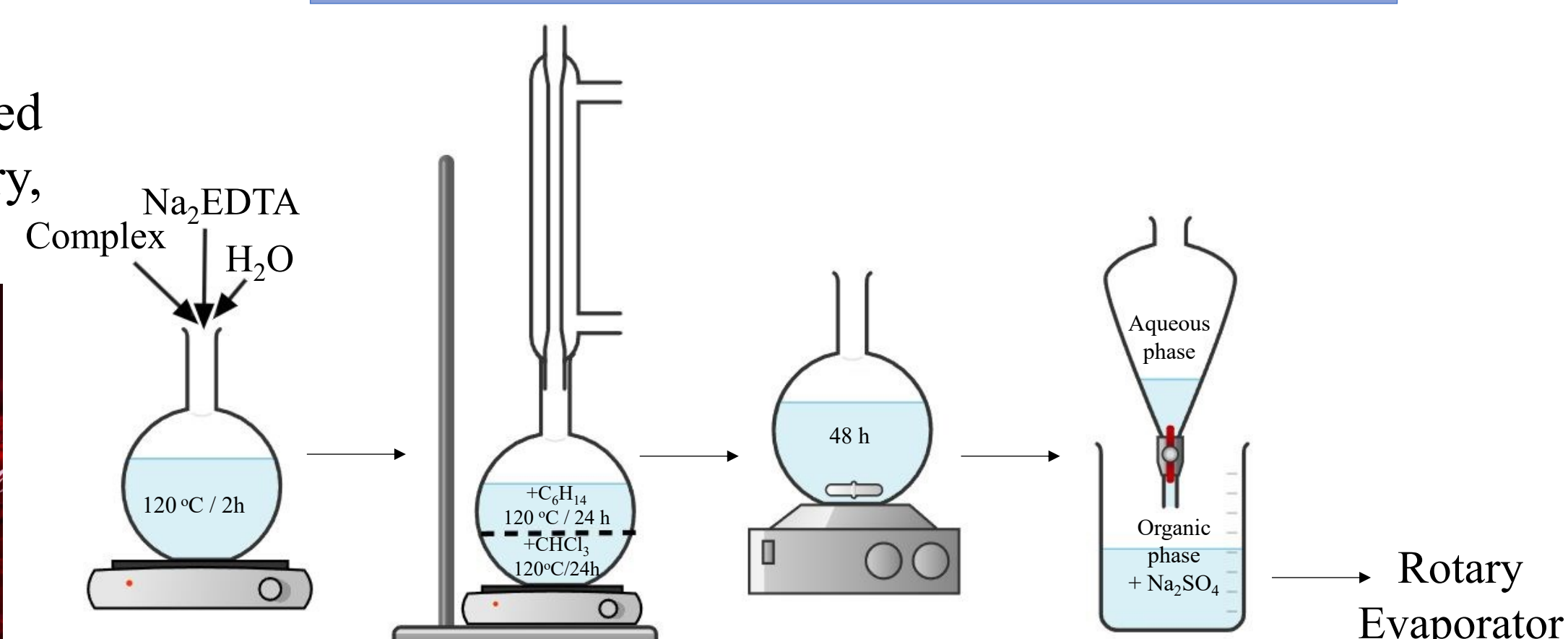


Fig. 2: Red crystals of crystalline product

Vanadium Extraction from the Complex



Results and Discussion

Red crystalline material (Fig. 2) was obtained the aforementioned synthesis, followed by crystallization using cold ethanol. Characterization proceeded through elemental analysis, FT-IR, Raman, NMR, ESI-MS UV-Visible, cyclic voltammetry, thermogravimetric analysis TGA-DTG, and X-ray crystallography (Fig. 2). The FT-IR spectra revealed the presence of vibrations of the newly generated and coordinated bis(2-pyridylcarbonyl)amine ligand with V(V) in the new compound. The observed vibrations are shifted to lower frequencies compared to the vibrations in the free 2-picolylamine, which indicates that there are changes in its vibrational state as vanadium reacts with it. The current research will be further extended to evaluate the efficiency of the newly synthesized materials in organic substrate catalytic transformation processes.

