

ABSTRACT

The aim of this thesis was to gain insight into the structure of the elusive trioxidane molecule (H_2O_3) and its derivatives by different methods of stabilization and subsequent structural characterization by single-crystal X-ray diffraction.

First, an optimized preparation of pure H_2O_3 solutions is presented and the use of molecular sieves as desiccants was investigated. It was shown that although these sieves effectively reduce the water content, they also contribute to the gradual degradation of H_2O_3 .

To gain structural insights into H_2O_3 in the solid state, various crystallization approaches were evaluated. Salts of weakly coordinating anions (WCAs) were tested for complex formation with trioxidane. Insight into the structure and stability of the hypothesized complexes was also gained through a preliminary DFT study.

In an effort to capture H_2O_3 by hydrogen bonding, organopnictogen(V) oxides were investigated as potential hydrogen-bond acceptors. A novel and efficient synthetic route for Ph_3AsO was developed, which led to a systematic crystallographic study of hydrogen-bonded cocrystals with this compound. Several new cocrystals of Ph_3AsO with H_2O_2 and *gem*-dihydroperoxides were obtained and structurally characterized. Hydrogen peroxide was shown to form a chair-like cocrystal arrangement, $[\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}_2]_2 \cdot \text{H}_2\text{O}_2$, stabilized by moderate hydrogen bonding, which increases its stability and allows potential use in organic oxidation reactions. This is the first systematic study of hydrogen-bonded cocrystals with Ph_3AsO , expanding the understanding of its chemistry and demonstrating its potential for crystal engineering.

The success of Ph_3AsO as a hydrogen-bond acceptor and coformer with H_2O_2 and *gem*-dihydroperoxides prompted us to investigate its hydrogen-bonding propensity towards H_2O_3 . The formation of hydrogen bonds enabled the crystallization of Ph_3AsO cocrystals with H_2O_3 . This is the first structure of *anti*- H_2O_3 in the solid-state bonded to two $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$ moieties. In addition, the stability of the adduct in solution was monitored by low-temperature NMR spectroscopy. The range of hydrogen-bond acceptors was extended to phosphine oxides, with Ph_3PO and Me_3PO leading to single crystals. In the cocrystal with Ph_3PO , trioxidane is present in its *syn* form. This is the first structural information about the less stable conformer of H_2O_3 . The bulkiness of the phenyl rings provides prolonged stability, so that a Raman spectrum of the crystal could be recorded at room temperature. However, the trioxidane molecule in both cocrystals was found to be disordered. Me_3PO proved to be the most suitable hydrogen-bond acceptor for

cocrystal formation, as trioxidane in this structure is well embedded as *anti*-H₂O₃ between the small Me₃PO molecules and the geometric parameters could be defined in detail.

In addition, an optimized synthetic route for the sterically shielding NHC ligand IPr** is reported. This ligand was used to synthesize a series of copper and silver complexes, including an air-sensitive hydrido complex capable of O₃ insertion.

Finally, the results of this work are of fundamental importance for the structural elucidation of short-lived, unstable, exotic molecules. In addition, low-temperature isolation and characterization techniques, which are relevant to a variety of scientific fields, were developed and perfected.

Keywords: trioxidane, crystal structure, cocrystals, hydrogen bonds, peroxides, NHC

