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Research paper

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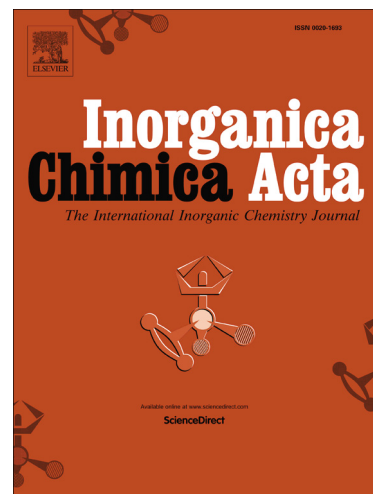
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Oxidation studies on mustard gas, and the first crystal structure of a metal-mustard gas complex

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ABSTRACT

Attempts to selectively oxidize mustard gas [(ClCH₂CH₂)₂S, abbreviated as BCES] to the non-toxic sulfoxide using a *trans*-Ru(TMP)(O)₂/O₂ catalyst (TMP = porphyrin dianion of 5,10,15,20-tetramesitylporphyrin) have led to isolation and characterization, including an X-ray structure, of *trans*-Ru(TMP)(BCES)₂, the first such report of a metal-mustard gas complex.

Keywords: Mustard Gas; Ruthenium porphyrins; Oxidations; X-ray structure

1. Introduction

About 30 years ago, reports from our group [1,2] presented studies on the catalyzed O₂-oxidation of thioethers to the sulfoxide, an industrial important process [3]. Ru^{II}-porphyrins were used as catalysts, and two very different mechanistic pathways were established depending on the porphyrin used, specifically OEP and TMP (the respective dianions of 2,3,7,8,12,13,17,18-octaethylporphyrin, and 5,10,15,20-tetramesitylporphyrin) [1,2,4,5]. The mechanism using the bis(thioether) species, Ru(OEP)(R₂S)₂ [6], involves a suggested initial 1e, ‘outer-sphere’ activation of O₂, with formation of Ru^{III} and superoxide that with acid (either added or present as impurity H₂O) forms the HO₂ radical that disproportionates into H₂O₂ and O₂; the H₂O₂ oxidizes the thioether to sulfoxide and the co-product H₂O then reduces the Ru^{III} back to Ru^{II} with co-production of the sulfoxide and the regeneration of the H⁺ co-catalyst [1,2]. The use of TMP (or OCP, the 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin dianion – see Fig.1) allowed for more ‘sterically hindered’ species, including formation (using O₂) of the corresponding *trans*-dioxo species Ru^{VI}(porp)(O)₂ [4,5] rather than the relatively inert, catalytically inactive, Ru^{IV}-O-Ru^{IV} species readily generated from OEP species [2]. These dioxo species are unique in being able to transfer catalytically both oxo ligands as O-atoms to organic substrates, including some thioethers [4]; such oxygenations have been well reviewed [7].

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