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Synthesis, structural evaluation and reactivity of newer peroxomolybdates and reaction mimics of vanadium bromoperoxidase

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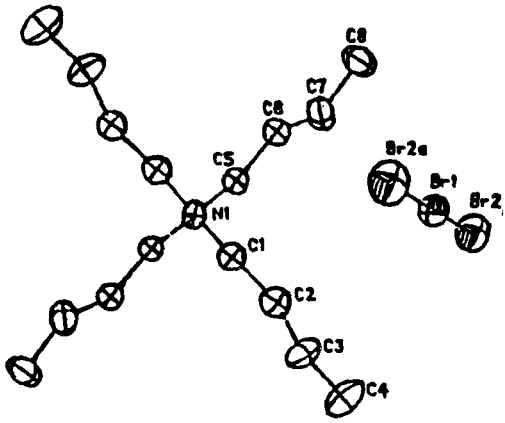
Newer peroxomolybdates of the types $A(NH_4)$ $[Mo_2O_3(O_2)_4(H_2O)_2]$. $2H_2O$, ($A = Na$(1) or K(2)), $A(NH_4)$ $[MoO(O_2)_2F_2].nH_2O]$. ($A = Na$, $n = 3$(3) or K, $n = 1$(4)), $(NH_4)_2[MoO(O_2)_2F_2].H_2O$(5), (NH_4) $[MoOF(O_2)_2L]$ (L = glycine(6), alanine(7) or valine(8)) and $NH_4)$ $[MoO(O_2)_2$(oxinate)] (9) have been synthesized. The results of a combination of chemical analyses, and IR, laser Raman, NMR, and electron absorption spectroscopies have been used for characterization and structural assessment. Oxidation of some selected organic and inorganic substrates involving 2, 4, 5 and 9 have been conducted. In an unprecedented reaction a solution of $H_2MoO_4.H_2O$ in H_2O_2 was interacted with NBu_4Br in aqueous solution to afford the tribromide NBu_4Br_3, with the Br_3^- being completely symmetric and linear. A CT-band at 267 nm ($\varepsilon = 52{,}000$) is characteristic of tribromide. The tribromide, NBu_4Br_3, is also obtained from similar reactions involving peroxo intermediates of Ti, VO^{3+} and UO_2^{2+}. Typically NBu_4Br_3 brominates phenol red to bromophenol blue, a reaction used to test the assay activity of vanadium bromoperoxidase. Biochemical implications (c.f. vanadium bromoperoxidase) have been highlighted.



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