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Syntheses, characterizatons and DNA photocleavage activities of some vanadium(V)-peroxo complexes

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Syntheses, Characterizations and DNA Photocleavage Activities of Some Vanadium(V)-Peroxo Complexes

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ABSTRACT

Ten oxodiperoxovanadates(V) of the formula $M[VO(O_2)_2(L\text{-}L)]$ or $M_3[VO(O_2)_2(L\text{-}L)]$ (where $M = NH_4^+$, K^+ or Na^+; L-L = 2,2'-dipyridyl, 4,4'-dimethyl-2,2-dipyridyl, 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline, 5-nitro-1,10-phenanthroline, 5-amino-1,10-phenanthroline, oxalate and diaqua) and six vanadium(V)-monoperoxo complexes, $NH_4[VO(O_2)(ida)]$, $K_2[VO(O_2)(nta)]$, $K_2[VO(O_2)(cit)]_2$, $H[VO(O_2)(pic)_2]$, $K[VO(O_2)(dipic)(H_2O)]$ and $[VO(O_2)(terpy)(H_2O)]ClO_4$ (where ida = iminodiacetate, nta = nitrilotriacetate, cit = citrate, pic = pyridine-2-carboxylate, dipic = pyridine-2,6-dicarboxylate and terpy = 2,2':6',2"-terpyridine) have been synthesized. Their DNA-photocleavage activities (illuminated at 365 nm), determined by a plasmid DNA-relaxation assay, were found to depend on their absorption spectral characteristics (e.g., molar absorptivity at 365 nm), their concentration and the illumination time. Results from experiments conducted in the presence of various reactive oxygen species (ROS) quenchers implicate singlet oxygen as the DNA-cleavage agent. No diminution of DNA-photocleavage activity was observed under quasi-anaerobic conditions, indicating that dissolved oxygen was not the source of the singlet oxygen. The production of singlet oxygen from the photolysis of some vanadium(V)-diperoxo complexes at 365 nm was confirmed, using two highly-sensitive singlet oxygen probes: 2,2,6,6-tetramethyl-4-piperidone, an EPR spin trap, and *trans*-1-(2'-methoxyvinyl)pyrene, a chemiluminescent probe. Metavanadate(V) anion, VO_3^-, was shown to be the vanadium photolysis product of the $[VO(O_2)_2(bpy)]^-$ anion using ^{51}V NMR spectroscopy. A mechanism for the photolysis of the $[VO(O_2)_2(bpy)]^-$ anion at neutral pH has been proposed. Furthermore, a cleaved

DNA fragment was analyzed by the Sanger dideoxy sequencing method. A sequence of 5'-ATC-3' was found to be associated with the site of photocleavage mediated by the $[VO(O_2)_2(5,6\text{-}Me_2phen)]^-$ ion.

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