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On the Existence of Triperoxo Vanadium Complexes. X-Ray Crystal Structures of $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O_2$ and of $(NH_4)[VO(O_2)_2(bipy)]\cdot 4H_2O$

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Triperoxo complexes are rare: the only examples authenticated by X-ray crystallography are $K[Nb(O_2)_3phen]\cdot 3H_2O$ and $K[Nb(O_2)_3phen]\cdot 3H_2O\cdot H_2O_2$ [1]. Vanadium triperoxo complexes have been claimed (salts of $[V(O_2)_3L]^-\cdot nH_2O$ (L = bipy, phen) or $[V(O_2)_3(C_2O_4)]^{3-}\cdot H_2O$ [2]). However, later work cast doubt on their existence, suggesting that they were in fact $[VO(O_2)_2L]^-$ and $[VO(O_2)_2(C_2O_4)]^{3-}\cdot 2H_2O$ [3], although these studies used an appreciably lower concentration of H_2O_2 in the preparation. We have therefore examined the crystal structure of '$K_3[V(O_2)_3(C_2O_4)]\cdot H_2O$' [1] and find the correct formula to be $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O_2$ [I] which is analytically indistinguishable from the triperoxo formulation. Our attempts to prepare '$(NH_4)[V(O_2)_3bipy]\cdot 3H_2O$' [2] gave $(NH_4)[VO(O_2)_2bipy]\cdot 4H_2O$ [II], and we have also studied its X-ray crystal structure.

Orange crystals of [I] and yellow crystals of [II] were prepared by the published methods [2]. X-ray data were collected on a Nicolet R3m/Eclipse S140 diffractometer system with monochromated Cu-Kα radiation. Data for [I]: $C_2H_2O_{11}K_3V$, monoclinic, a = 7.073(2), b = 8.080(2), c = 17.391(2) Å, β = 96.63(2), U = 987.3(4) Å^3 (at 18 °C), space group $P2_1/c$ and Z = 4. A total of 1329 independent reflections measured (to θ = 57°), of which 127 were judged to be 'unobserved'. Data for [II]: $C_{10}H_{20}O_9N_3V$, monoclinic, a = 7.114(1), b = 18.142(2), c = 12.845(1) Å, β = 90.52(1), U = 1657.8(3) Å^3 (at 18 °C), space group $P2_1/n$ and Z = 4. (We have been informed that a similar result has been obtained concurrently for [II] [4]). A total of 2197 independent reflections measured (to θ = 57°), of which 153 were judged to be 'unobserved'.

Both structures were solved by Patterson and Fourier methods, and least-squares refinement has reduced R to 0.036 and 0.039 respectively. The program system SHELXTL [5] was used throughout the calculations.

The results show conclusively that [I] is a perhydrate of formula $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O_2$, and that the anion (Fig. 1) is structurally very similar to that in [II] (Fig. 2). The anion in [I] is pentagonal bipyramidal with two somewhat asymmetrically bonded peroxo groups (mean V–O, 1.923(3) and 1.876(3) Å; mean O–O, 1.466(4) Å) and one oxygen atom (V–O, 2.062(3) Å) from an oxalate group constituting the pentagonal plane. The apical positions are occupied by the other oxygen atom of the bidentate oxalate group (V–O, 2.249(3) Å) and by the V=O (1.620(3) Å). The H_2O_2 of crystallisation is hydrogen bonded, to a peroxo oxygen atom and to a terminal oxygen atom in the oxalate ligand of an

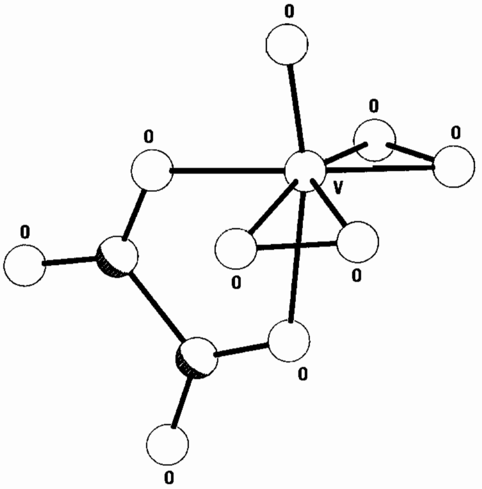

Fig. 1. Structure of the pentagonal bipyramidal ion $[VO(O_2)_2(C_2O_4)]^{3-}$.

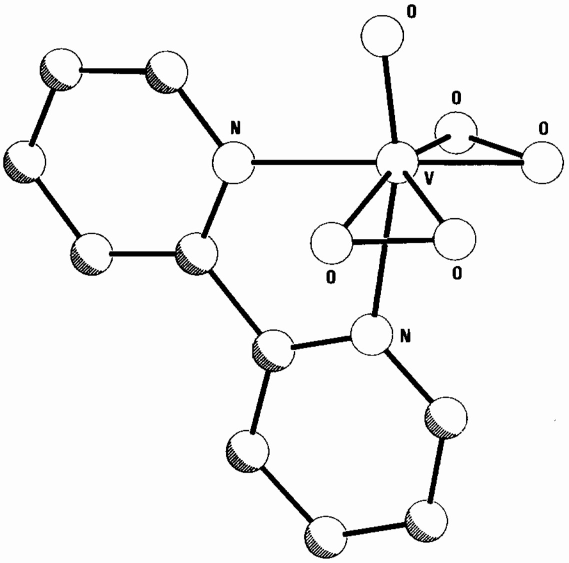

Fig. 2. Structure of the $[VO(O_2)_2(bipy)]^-$ ion.

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adjacent anion. The H_2O_2 moiety has a skew conformation with a dihedral angle of 136°.

The structure of the anion of [II] is similar; the two peroxo groups are again somewhat asymmetrically bound (mean V–O, 1.912(2) and 1.875(2) Å; mean O–O, 1.467(3) Å), the remaining equatorial and one axial position being occupied by the chelating bipyridyl ligand (equatorial V–N, 2.151(2) Å; axial V–N, 2.295(2) Å), while the other axial position has V=O at 1.612(2) Å. Both [I] and [II] are structurally very similar to other vanadium diperoxo species, *e.g.* $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$ [6].

The infrared spectra of [I] and [II] are fully in accordance with the formulations as $[VO(O_2)_2\text{-}L]^{n-}$ species. The O–O stretching bands lie at 878 and 856 cm^{-1} in [I] and at 880 and 860 cm^{-1} in [II]. The V=O stretches are at 933 and 930 cm^{-1} in [I] and [II] respectively. Since all the 'triperoxo' complexes reported [2] have bands near 930 cm^{-1} and 880 cm^{-1} we conclude that they all contain the $[VO(O_2)_2]$ moiety. We find that O–H stretching vibrations in [I], associated with the hydrogen peroxide of crystallisation, are at 3550 cm^{-1} and 2775 cm^{-1}; these we associate with the ν_1 and ν_5 vibrations observed in other perhydrates [7].

The reaction of $[VO_4]^{3-}$ with excess oxalic acid and a larger excess of H_2O_2 [2] gives the perhydrate [I], while a lower concentration of H_2O_2 gives hydrates [3, 6]. In the case of the bipyridyl complex, a lower $V:H_2O_2$ reacting ratio is used in the preparation [2] and the resulting product is a hydrate [II]. We conclude that the concentration of H_2O_2 used in such preparations is the controlling factor in determining whether hydrates, perhydrates, or mixtures of both are formed.

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