Synthesis and physico-chemical studies of newer mono and diperoxo heteroligand complexes of vanadium

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The synthesis of monoperoxo-vanadium(V) complexes, [VO(O₂)QL] (Q = 8-quinolinolate and L = EtOH, DMF, DMSO, or THF), and diperoxovanadates(V), A₃[VO(O₂)₂(HPO₄)] · 2H₂O (A = K or NH₄) are described. While the [VO(O₂)QL] complexes have been synthesized from the reaction of V₂O₅ with H₂O₂ and a solution of 8-quinolinol in different donor solvents (L) at pH ca. 2, the oxodiperoxo(hydrophosphato) vanadate(V) dihydrates, A₃[VO(O₂)₂-(HPO₄)] · 2H₂O, have been prepared from the reaction of V₂O₅ with H₂O₂ and phosphoric acid at pH 6 of the reaction medium. The compounds have been characterized by chemical analyses, magnetic susceptibility, and molar conductance measurements, and by IR, laser Raman, ¹H NMR, and electronic spectroscopic studies. Evidence has been provided for triangularly bonded peroxide (O₂²⁻) and coordinated heteroligands. The existence and stability of the complex [VO(O₂)₂(HPO₄)]³⁻ in solution have been ascertained from solution Raman spectroscopy and conductance measurements.

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On décrit la synthèse des complexes monoperoxo–vanadium(V), [VO(O₂)QL] (Q = 8-quinoléinolate et L = EtOH, DMF, DMSO ou THF) et diperoxovanadates(V), A₃[VO(O₂)₂(HPO₄)]·2H₂O (A = K ou NH₄). Alors que les complexes [VO(O₂)QL] ont été synthétisés par la réaction du V₂O₅ avec du H₂O₂ et une solution du 8-quinoléinol dans divers solvants donneurs (L), à un pH d'environ 2, les dihydrates de l'oxodiperoxy(hydrophosphato)vanadate A₃[VO(O₂)₂(HPO₄)]·2H₂O ont été préparés par la réaction du V₂O₅ avec le H₂O₂ et de l'acide phosphorique, au pH de 6 du milieu réactionnel. On a caractérisé les produits par des analyses chimiques, par des mesures de susceptibilité magnétique et de conductivité molaire et par des études spectroscopiques IR, Raman au laser, RMN du ¹H et électroniques. On a obtenu des données relatives au peroxyde (O₂²⁻) lié d'une façon triangulaire et aux hétéroligands qui sont coordonnés. Sur la base de la spectroscopie Raman et des mesures de conductivité, on a établi l'existence et la stabilité du complexe [VO(O₂)₂(HPO₄)]³⁻ en solution.

[Traduit par la rédaction]

Introduction

Peroxo-vanadium systems are important for a variety of reasons including their role in oxidation catalysis (1,2) and biochemical relevance (3–9). Suitable heteroligands are known to bring about stability to such systems enabling isolation in the solid state, for instance, NH₄[VO(O₂)₂-(C₁₀H₈N₂)], which was synthesized by Vuletic and Djordjevic (10) and crystallographically characterized by Szentivanyi and Stomberg (11). In addition, the synthesis and structural assessment of several NO-donor–peroxo-vanadium(V) complexes with pyridine-2-carboxylate (1, 12), pyrazine-2-carboxylate (1), pyridine-2,6-dicarboxylate (13), iminodiacetate (14), and N-(2-oxidophenyl)salicylidinaminate (2) as the heteroligands are notable contributions to the domain of peroxo-chemistry of the metal. Over the past few years, we have been working in this area (15, 16) and our major emphasis has been on the development of newer synthetic methodologies as well as to synthesize new compounds. The selection of heteroligands is important and the coligands chosen for the present studies include 8-quinolinol and phosphate. While the importance of 8-quinolinol as a ligand has already been emphasized (17, 18), our concern with phosphate was to ascertain if it would form a peroxo(phosphato)vanadium(V) species. Such a complex is expected to be of considerable interest in the context of the vanadate–phosphate antagonism in physiology and the use

of phosphate buffers in the reconstitution of vanadium bromoperoxidase. Since a citrate/phosphate buffer was used in the purification process of bromoperoxidases (3, 4, 19) containing vanadium(V), the possibility of phosphate coordination with a peroxovanadate(V) cannot be ruled out. Indeed, there has been definite evidence to support the formation of a mononuclear monophosphato–vanadium complex in aqueous solutions (20, 21).

In this paper, the synthesis and physico-chemical characterization of complexes of the type [VO(O₂)QL] (Q = 8-quinolinolate and L = EtOH, DMSO, DMF, or THF) and A₃[VO(O₂)₂(HPO₄)] · 2H₂O (A = NH₄ or K) are presented. Also reported here are the results of solution Raman and conductance experiments in support of the existence and stability of the complex [VO(O₂)₂(HPO₄)]³⁻ ion in solution.

Experimental

The chemicals used were all reagent grade products. The IR spectra were recorded on a Perkin Elmer model 983 spectrophotometer. The laser Raman (LR) spectra were recorded at ambient temperatures on a SPEX Ramalog model 1403 spectrometer using the line at 6471 Å of a Krypton laser from a Coherent model Innova 90-K(UV) as the excitation source. The UV–visible spectra were recorded in water or DMF solutions on a Hitachi model 330 spectrophotometer. Molar conductances were measured either in conductivity grade water or in DMF using a Systronics type 304 digital direct-reading conductivity bridge. The pH values of the reaction solutions were measured with a Systronics type 335 digital pH meter and also with pH indicator paper (BDH). The ¹H NMR spectra were recorded in deuterated DMSO using a Varian 390 90-MHz spectrometer. Tetramethyl silane (TMS) was used as the internal standard. Carbon, hydrogen, and nitrogen were determined by microanalytical methods (Micro-Analysis Lab., Depart-

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ment of Chemistry, NEHU, Shillong-793003). Vanadium, peroxide, and phosphate were estimated by the methods given in our earlier papers (15, 22).

Synthesis of oxoperoxo-8-quinolinolatovanadium(V) complexes,
  [VO(O₂)QL] (Q = 8-quinolinolate, L = EtOH, DMSO,
  DMF, or THF)

As the methods of synthesis of $[VO(O_2)QL]$ compounds are similar, only a representative procedure is described.

V_2O_5 (1 g, 5.49 mmol) was first dissolved in 30% hydrogen peroxide (15 cm³, 132.36 mmol) to obtain a red solution with liberation of heat. To this was added a solution of 8-quinolinol (1.6 g, 11.02 mmol), made up separately in each of the following donor solvents (100 cm³), EtOH, DMSO, DMF, or THF, with continuous stirring. The concentration ratio of V:8-quinolinol: H_2O_2 was 1:2:24.1. No colour change or heat liberation was apparent. The reaction mixture was stirred for ca. 30 min in an ice-bath, whereupon a brick-red microcrystalline solid separated out. The pH value of the solution was recorded to be ca. 2. The solid oxoperoxo-8-quinolinolato-vanadium(V) complex $[VO(O_2)$-QL] (Q = 8-quinolinolate, L = EtOH, DMSO, DMF, or THF) was filtered off, washed three or four times with ethanol, and finally dried *in vacuo* over concentrated H_2SO_4. The yields of $[VO(O_2)$-Q(EtOH)]$, $[VO(O_2)Q(DMSO)]$, $[VO(O_2)Q(DMF)]$, and $[VO$-$(O_2)Q(THF)]$ were 2.6 g (82%), 2.8 g (80%), 2.9 g (85%), and 2.7 g (78%), respectively.

Anal. calcd. for $[VO(O_2)Q(EtOH)]$: V 17.62, $O_2{}^{2-}$ 11.07, C 45.7, N 4.84, H 4.15; found: V 17.28, $O_2{}^{2-}$ 10.85, C 45.56, N 4.96, H 4.2. ¹H NMR (DMSO-d_6) δ: 8.85 (d,H), 8.7 (d,H), 7.8(d,H), 7.6(d,H), 7.4(d,H), 7.15(d,H), 3.43(q,2H), 2.5(s,H), 1.06(t,3H).

Anal. calcd. for $[VO(O_2)Q(DMF)]$: V 16.11, $O_2{}^{2-}$ 10.12, C 45.59, N 8.85, H 4.11; found: V 15.98, $O_2{}^{2-}$ 10.2, C 45.92, N 9.03, H 4.12. ¹H NMR (DMSO-d_6) δ: 8.82(d,H), 8.65(d,H), 7.76(d,H), 7.59(d,H), 7.35(d,H), 7.13(d,H), 7.93(s,H), 2.83(s,3H), 2.7(s,3H).

Anal. calcd. for $[VO(O_2)Q(DMSO)]$: V 15.86, $O_2{}^{2-}$ 9.96, C 41.14, N 4.35, H 3.73; found: V 15.62, $O_2{}^{2-}$ 9.81, C 42.10, N 4.42, H 3.78. ¹H NMR (DMSO-d_6) δ: 8.86(d,H), 8.7(d,H), 7.85(d,H), 7.68(d,H), 7.38(d,H), 7.10(d,H), 2.3(s,6H).

Anal. calcd. for $[VO(O_2)Q(THF)]$: V 16.16, $O_2{}^{2-}$ 10.15, C 49.55, N 4.44, H 4.44; found: V 15.94, $O_2{}^{2-}$ 9.85, C 50.11, N 4.54, H 4.38. ¹H NMR (DMSO-d_6) δ: 8.82(d,H), 8.65(d,H), 7.79(d,H), 7.58(d,H), 7.25(d,H), 7.11(d,H), 3.60(m,4H), 1.73(m,4H).

Synthesis of ammonium and potassium oxodiperoxo-
  (hydrophosphato)vanadate(V) dihydrates,
  A₃[VO(O₂)₂(HPO₄)] · 2H₂O (A = NH₄ or K)
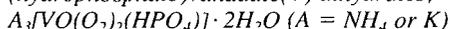
In a typical procedure, a mixture of vanadium pentoxide (1 g, 5.49 mmol) and 88% phosphoric acid (1 cm³, 17.85 mmol, density 1.75 g cm⁻³) was reacted with 30% hydrogen peroxide (15 cm³, 132.36 mmol) in an ice-bath with stirring. A clear red solution thus obtained was stirred for ca.15 min followed by the addition of aqueous ammonia (specific gravity 0.9) or 20% KOH solution until the reaction medium attained a pH value of 6 with its colour turning to yellow. An addition of ethanol to this precipitated out a yellow microcrystalline product. The compound was filtered off, washed two or three times with ethanol, and finally dried *in vacuo* over concentrated H_2SO_4. The yield of $(NH_4)_3[VO(O_2)_2(HPO_4)] · 2H_2O$ was 2.82 g (81%) and that of $K_3[VO(O_2)_2(HPO_4)] · 2H_2O$ was 3.17 g (76%). Anal. calcd. for $(NH_4)_3[VO(O_2)_2(HPO_4)] · 2H_2O$: V 16.07, $O_2{}^{2-}$ 20.19, $PO_4{}^{3-}$, 29.96, N 13.25, H 5.36; found: V 15.92, $O_2{}^{2-}$ 20.1, $PO_4{}^{3-}$ 29.21, N 13.11, H 5.32. Anal. calcd. for $K_3[VO(O_2)_2(HPO_4)] · 2H_2O$: V 13.39, $O_2{}^{2-}$ 16.83, $PO_4{}^{3-}$ 24.97, H 1.31; found: V 13.13, $O_2{}^{2-}$ 16.3, $PO_4{}^{3-}$, 25.25, H 1.38.

Results and discussion

Vanadium has a strong affinity for peroxide $(O_2{}^{2-})$ and the composition of a peroxo-vanadium species is pH dependent

(15, 16, 23–26). The number of coordinated $O_2{}^{2-}$ generally increases as the solution pH value is raised. In one of the present reactions, the interaction of V_2O_5 with hydrogen peroxide and a solution of 8-quinolinol (QH) in each of the donor solvents (L) (L = EtOH, DMSO, DMF, or THF) was conducted at pH 2. This led to the synthesis of new heteroligand monoperoxovanadium(V) compounds of the type $[VO(O_2)QL]$ in very high yields. QH was dissolved in the chosen organic solvents (L) so that an option for the formation of quaternary complexes existed. Since monoperoxo complexes of the metal are far less frequently encountered, it was one of our concerns to improvise a route to such species. Accordingly, the pH value of ca. 2 attained spontaneously was not raised so that the goal could be achieved. In contrast, the successful synthesis of complex peroxovanadates(V) containing $HPO_4{}^{2-}$ as the heteroligand was possible from the reaction of V_2O_5 with phosphoric acid (H_3PO_4) and H_2O_2, only when the pH value was raised to 6. The products isolated at pH values < 6, though containing both peroxide and phosphate, were inconsistent in regard to their compositions. A comparatively higher pH value is believed to have directed the formation of the ternary diperoxovanadate(V), $[VO(O_2)_2(HPO_4)]]^{3-}$. The complex was isolated as $A_3[VO(O_2)_2(HPO_4)] · 2H_2O$ (A = K or NH₄) by the addition of ethanol, which facilitated the precipitation. The alkali used to raise the pH of the solution served also as a source of the counter-cation $NH_4{}^+$ or K^+ (A^+). The occurrence of an acid phosphate, $HPO_4{}^{2-}$, can be rationalized in terms of the pH value maintained in the synthesis.

Both the brick-red $[VO(O_2)QL]$ and the yellow $A_3[VO$-$(O_2)_2(HPO_4)] · 2H_2O$ were obtained as microcrystalline products. They are insoluble in nonpolar organic solvents. While the former is insoluble in water, but soluble in polar organic solvents like DMF and DMSO, the latter is soluble only in water. The compounds are stable for a prolonged period and are capable of being stored in closed sample containers. Both the mono- and the diperoxo compounds reported herein are diamagnetic in nature in conformity with the oxidation state of the metal. The molar conductances of $[VO(O_2)QL]$ recorded in DMF and those of $A_3[VO(O_2)_2(HPO_4)] · 2H_2O$ recorded in water were found to lie in the ranges 5–10 Ω^{-1} cm² mol⁻¹, and 370–380 Ω^{-1} cm² mol⁻¹, respectively, in agreement with their formulae. Furthermore, the results of conductance measurements, obtained over a period of 10 days at an interval of 24 h each, were practically similar to those recorded on freshly prepared solutions. This clearly attests to the stability of the compounds in the respective solutions.

Each of the monoperoxo-vanadium(V) and diperoxovanadate(V) complexes exhibited a characteristic spectral pattern in the infrared region. The significant general features are the absorptions at ca. 950, ca. 855, ca. 620, and ca. 580 cm⁻¹ assigned to $\nu(V{=}O)$, $\nu(O{-}O)$ (ν_1), $\nu(V{-}O_2)(\nu_2)$, and $\nu(V{-}O_2)(\nu_3)$, respectively (15, 16, 27). The occurrence of bands at ca. 855 cm⁻¹, ca. 620, and ca. 580 cm⁻¹ clearly indicates the presence of triangularly bonded (C_{2v}) peroxide (15, 16, 27). In addition to the features originating from VO^{3+} and coordinated peroxide, the monoperoxo complexes $[VO(O_2)QL]$ show bands due to the coordinated 8-quinolinolate ligand(Q) with the pattern comparing very well with that reported (17, 28) for the 8-quinolinolato coordinated systems. Moreover, the IR spectra of $[VO(O_2)$-Q(DMSO)]$ and $[VO(O_2)Q(DMF)]$ exhibit strong bands at 940 cm⁻¹ $(\nu(S{=}O))$ (29) and at 1650 cm⁻¹ $(\nu(C{=}O))$ (30),

TABLE 1. Comparison of peroxo stretching frequencies [v(O—O)] for the complexes to those of previously reported compounds from this laboratory

| Compound | v(O—O) (cm^{-1}) | | Reference |
	IR	Raman	
$K_2[V(O_2)_3F]$	855s		15a
$K_2[VO(O_2)_2F]$	870s⎱ 890s⎰		32
$K_2[V(O_2)_3Cl]$	855s		15b
$K_2[VO(O_2)_2Cl]$	875s⎱ 890s⎰		15b
$K_3[VO(O_2)_2CO_3] \cdot 3H_2O$	865s	865s	33
$K[VO(O_2)_2en]$	870s	880	34
$K[VO(O_2)_2(H_2O)]$	860s	870	16a
$K[VO(O_2)_2GlyH]$	850s		16b
$K_2[V_2O_2(O_2)_3(cysH)_2] \cdot H_2O$	851s⎱ 818m⎰		35
$[VO(O_2)Q(EtOH)]$	855s		
$[VO(O_2)Q(DMF)]$	850s		
$[VO(O_2)Q(DMSO)]$	850s		This
$[VO(O_2)Q(THF)]$	855s		work
$K_3[VO(O_2)_2(HPO_4)] \cdot 2H_2O$	865s	857	
$(NH_4)_3[VO(O_2)_2(HPO_4)] \cdot 2H_2O$	860s	860	

Abbreviations: en = ethylenediamine, Q = 8-quinolinolate, GlyH = glycine, cysH = cysteinate, EtOH = ethyl alcohol, DMF = dimethylformamide, DMSO = dimethyl sulphoxide, THF = tetrahydrofuran.

respectively. The presence of distinct bands at 940 and 1650 cm^{-1} suggests that the DMSO and DMF are bonded to the metal centre through their O-atoms in the respective cases (29, 30). The bands due to the coordinated EtOH and THF in the complexes [VO(O$_2$)QL] (L = EtOH or THF) could not be identified because of their overlap with those of the 8-quinolinolato ligand.

In addition to the bands due to V=O and coordinated O$_2{}^{2-}$, the IR spectra of A$_3$[VO(O$_2$)$_2$(HPO$_4$)] · 2H$_2$O(A = NH$_4$ or K) display a strong but broad absorption in the region 1010–1160 cm^{-1} and a medium intensity broad absorption at 2800–2900 cm^{-1}. These resemble, in their shapes and positions, those observed for the coordinated hydrophosphate group (HPO$_4{}^{2-}$) (31) and lend support to the contention. The signals at ca. 960, ca. 860, ca. 630, and ca. 580 cm^{-1} due to the v(V=O), v(O—O)(v_1), v(V—O$_2$)(v_2), and v(V—O$_2$)(v_3) modes, respectively, observed in the laser Raman spectra of the compounds, complement the corresponding IR modes. The additional bands at ca. 1640 s, and ca. 3500 s, br cm^{-1} in the IR spectra of the complexes represented the δ(H—O—H) and v(O—H) modes of uncoordinated water (ref. 29, p. 228). A comparison of the vibrational spectra of the newly synthesized compounds with those of some of our previously reported peroxo-vanadium(V) complexes (15, 16, 32–35) causes us to state that the most significant band [v(O—O)], characteristic of the bound peroxides, does not appear to show any remarkable variation in its position with changes in the metal coordination sphere (Table 1). The v(O—O) bands lie in the region 850–890 cm^{-1} in the IR spectra, while similar modes occur between 855 and 880 cm^{-1} in the Raman spectra of the compounds so far investigated by us. In other words, the vibrational spectra of the coordinated peroxide seem to be independent of the nature of the heteroligands present in the complex peroxo-vanadium(V) species.

From the biochemical point of view, the peroxo(hydrophosphato)-vanadate(V) complex, [VO(O$_2$)$_2$(HPO$_4$)]$^{3-}$, is of considerable interest. To furnish evidence for its existence in solution, we sought to show that the use of laser Raman (LR) spectroscopy provided very valuable information in this regard. The LR spectrum of the yellow solution of V$_2$O$_5$, phosphoric acid, and H$_2$O$_2$ at pH 6 adjusted by the addition of KOH solution (vide Experimental) was recorded before isolating the compound. The spectrum exhibited polarized bands at 972, 865, and at 565 cm^{-1} due to v(V=O), v(O—O)(v_1), v_s(V—O$_2$)(v_3), respectively, and a depolarized band at 630 cm^{-1} assigned to v_{as}(V—O$_2$)(v_2). The LR spectral pattern of the corresponding solid K$_3$[VO(O$_2$)$_2$(HPO$_4$)], including the positions of the Raman signals, was similar to the above with its v(V=O), v(O—O)(v_1), v_s(V—O$_2$)(v_3), and v_{as}(V—O$_2$)(v_2) occurring at 970, 857, 575, and 630 cm^{-1}, respectively. Furthermore, the LR spectrum of a freshly prepared solution of K$_3$[VO(O$_2$)$_2$(HPO$_4$)] exhibited these bands at positions very close in wave numbers to the LR bands observed for the solution prior to isolating the complex, as well as to bands for the solid K$_3$[VO(O$_2$)$_2$(HPO$_4$)] as discussed above. Equally significant is the consistent appearance of a very strong but broad signal with its peak at ca. 1065 cm^{-1} in each of the three spectra recorded for the complex under consideration. The band, in terms of its shape and position, compares very well to the corresponding IR band of the coordinated HPO$_4{}^{2-}$ observed for the solid K$_3$[VO(O$_2$)$_2$(HPO$_4$)], thereby lending further credence to the contention. These results attest not only to the existence but also to the stability of the complex [VO(O$_2$)$_2$(HPO$_4$)]$^{3-}$ species in solution, at least under the present experimental conditions.

The electronic spectra of [VO(O$_2$)QL] complexes in DMF showed two bands, one each at ca. 268 (ε = 1.525 × 10^4 L mol^{-1} cm^{-1}) and at 360–410 (broad) nm (ε = 2 × 10^3 L

mol^{-1} cm^{-1}). While the former has been assigned to the internal transition ($\pi-\pi^*$) of the 8-quinolinolate ligand (28), the latter probably owes its origin to a combination of a peroxo (LMCT) and the internal ($\pi-\pi^*$) transition of the 8-quinolinolato ligand. The UV–visible spectra of the diperoxo compounds $A_3[VO(O_2)_2(HPO_4)] \cdot 2H_2O$ (A = NH_4 or K), recorded in water, exhibited only one (LMCT) band at 320 nm. The transition at 320 nm is similar to that of the other diperoxovanadium compounds containing triangularly bonded peroxide (36).

The ^1H NMR spectra of the monoperoxovanadium(V) complexes, $[VO(O_2)QL]$, were recorded in DMSO-d_6 solvent. The significant features of the NMR spectra are the signals due to the coordinated 8-quinolinolato ligand and the coordinated L (L = EtOH, DMF, or THF). The signals due to coordinated 8-quinolinolato ligands, observed at δ values ca. 8.9, ca. 8.7, ca. 7.8, ca. 7.6, ca. 7.4, and ca. 7.2, are similar to those previously reported for the 8-quinolinolato-vanadium complexes (17, 37, 38). Apart from these, the signals due to the coordinated ethanol appear at δ 1.06(t), 2.5(s), and 3.43(q) originating from -CH_3, O-H and, -CH_2-, respectively (39). The DMF signals, for L = DMF, were observed at δ 7.93(s), 2.83(s), and 2.7(s) assigned to HCO-, -CH_3, and -CH_3, respectively (ref. 39, p. 344). The THF signals of the corresponding complex appear at δ 1.73(m) and 3.6(m) due to -CH_2-CH_2- and -CH_2-O-CH_2-, respectively (ref. 39, p. 348). Thus, the ^1H NMR results show conclusively that the 8-quinolinolato ligand is bonded to the metal center. The results are consistent with the presence of a metal–oxygen covalent bond and a long labile V—N bond (17). The chemical shifts agree with this proposition. The NMR spectroscopic studies also suggest that each of the L molecules, i.e., EtOH, DMF, and THF, is bonded to the metal center.

Acknowledgements

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