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), A2[V(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, A2[V(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 trianually 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.


On décrit la synthèse des complexes monoperoxo-vanadium(V), [VO(O2)QL] (Q = 8-quinolinolinate et L = EtOH, DMF, DMSO ou THF) et diperoxovanadates(V), A2[V(O2)2(HPO4)]·2H2O (A = K ou NH4). Alors que les complexes [VO(O2)QL] ont été synthétisés par la réaction du V2O5 avec H2O2 et une solution du 8-quinolénone dans divers solvants donneurs (L), à un pH d'environ 2, les dihydrates de l'oxodiperoxo(hydrophosphato)vanadate A2[V(O2)2(HPO4)]·2H2O ont été préparés par la réaction du V2O5 avec 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[V(O2)2(C10H4N2)] 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 ligands 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(phosphate)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 monophospho-vanadate 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-quinolinolinate and L = EtOH, DMF, DMSO, or THF) and A2[V(O2)2(HPO4)]·2H2O (A = NH4 or K) are described. 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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Vanadium can exist in different oxidation states and coordination geometries, which affect its properties and reactivity. The synthesis and study of vanadium complexes are important for understanding their potential applications in various fields, including catalysis, magnetism, and medicinal chemistry.

The synthesis of vanadium complexes often involves the use of strong oxidizing agents like hydrogen peroxide, which can lead to the formation of peroxo and peroxo-bridged complexes. These complexes exhibit unique spectral properties and can be characterized using techniques such as infrared spectroscopy.

In the case of vanadium complexes containing peroxo ligands, the IR spectra show characteristic bands at around 940 cm⁻¹ and 580 cm⁻¹, which correspond to the vibrations of the coordinated peroxo groups. These bands are useful for identifying the presence of peroxo ligands in the complex.

The results of vanadium complex synthesis and characterization are crucial for the development of new materials and catalysts. For instance, vanadium-based catalysts can be used in the production of fuels, pharmaceuticals, and other chemicals. Understanding the properties of vanadium complexes is essential for optimizing their performance in these applications.

In conclusion, the synthesis and characterization of vanadium complexes with peroxo ligands are important areas of research that have potential applications in various fields. Further studies in this area could provide new insights into the properties and behavior of vanadium complexes, leading to the development of new materials and technologies.
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\(_2\)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 \(\text{A}_3[\text{VO(O,)}_2\text{HPO}_4]\cdot 2\text{H}_2\text{O}\) (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 hydroxophosphate group (HPO\(_4^{3-}\)) (31) and lend support to the contention. The signals at ca. 960, ca. 860, ca. 630, and ca. 580 cm\(^{-1}\) due to the \(v(\text{V}=\text{O}), v(\text{O}–\text{O})(v_1), v(\text{V}=\text{O})(v_2), \) and \(v(\text{V}=\text{O})(v_3)\) 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 \(\delta(\text{H}–\text{O}–\text{H})\) and \(v(\text{O}–\text{H})\) 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 \(v(\text{O}–\text{O})\), characteristic of the peroxo dioxides, does not appear to show any remarkable variation in its position with changes in the metal coordination sphere (Table 1).

The \(v(\text{O}–\text{O})\) 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 peroxy 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(hydrophospho)-vanadate(V) complex, [VO(O,)(HPO,)]\(^{3-}\), 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 \(v(V=O), v(\text{O}–\text{O})(v_1), v(\text{V}=\text{O})(v_2), \) and \(v(\text{V}=\text{O})(v_3)\) respectively, and a depolarized band at 630 cm\(^{-1}\) assigned to \(v_{\text{as}}(\text{V}–\text{O})\)(v\(_2\)). The LR spectral pattern of the corresponding solid \(\text{K}_3[\text{VO(O,)}_2\text{HPO}_4]\), including the positions of the Raman signals, was similar to the above with its \(v(\text{V}=\text{O}), v(\text{O}–\text{O})(v_1), v(\text{V}=\text{O})(v_2), \) and \(v_{\text{as}}(\text{V}–\text{O})\)(v\(_2\)) occurring at 970, 857, 575, and 630 cm\(^{-1}\), respectively. Furthermore, the LR spectrum of a freshly prepared solution of \(\text{K}_3[\text{VO(O,)}_2\text{HPO}_4]\) 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 \(\text{K}_3[\text{VO(O,)}_2\text{HPO}_4]\) 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\(_4^{3-}\) observed for the solid \(\text{K}_3[\text{VO(O,)}_2\text{HPO}_4]\), 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,)(HPO,)]\(^{3-}\) species in solution, at least under the present experimental conditions.

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

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### Table 1. Comparison of peroxy stretching frequencies \([v(\text{O}–\text{O})]\) for the complexes to those of previously reported compounds from this laboratory

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (cm(^{-1}))</th>
<th>Raman (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{F}])</td>
<td>855s</td>
<td></td>
<td>15a</td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{F}])</td>
<td>870s</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{Cl}])</td>
<td>890s</td>
<td></td>
<td>15b</td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{Cl}])</td>
<td>855s</td>
<td></td>
<td>15b</td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}])</td>
<td>865s</td>
<td>865s</td>
<td>33</td>
</tr>
<tr>
<td>(\text{K}[\text{VO(O,)}_2\text{en}])</td>
<td>870s</td>
<td>880</td>
<td>34</td>
</tr>
<tr>
<td>(\text{K}[\text{VO(O,)}_2\text{H}_2\text{O}])</td>
<td>860s</td>
<td>870</td>
<td>16a</td>
</tr>
<tr>
<td>(\text{K}[\text{VO(O,)}_2\text{GlyH}])</td>
<td>850s</td>
<td></td>
<td>16b</td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{(cysH)}_2 \cdot \text{H}_2\text{O}])</td>
<td>851s</td>
<td>818s</td>
<td>35</td>
</tr>
<tr>
<td>([\text{VO(O,)}_2\text{Q(EIOH)}])</td>
<td>855s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{VO(O,)}_2\text{Q(DMIF)}])</td>
<td>850s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{VO(O,)}_2\text{Q(DMSO)}])</td>
<td>850s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{VO(O,)}_2\text{Q(THF)}])</td>
<td>855s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{K}_3[\text{VO(O,)}_2\text{(HPO,)}] \cdot 2\text{H}_2\text{O})</td>
<td>865s</td>
<td>857</td>
<td></td>
</tr>
<tr>
<td>((\text{NH}_2)_2[\text{VO(O,)}_2\text{(HPO,)}] \cdot 2\text{H}_2\text{O})</td>
<td>860s</td>
<td>860</td>
<td></td>
</tr>
</tbody>
</table>

**Abbreviations:** en = ethylenediamine, Q = 8-quinolinolinate, GlyH = glycine, cysH = cysteinate, EtOH = ethyl alcohol, DMF = dimethylformamide, DMSO = dimethyl sulfoxide, THF = tetrahydrofuran.
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-quinolinolate ligand. The UV-visible spectra of the diperoxo compounds $\text{A}_2[\text{VO(O}_2)_2(\text{HPO}_3)_2] \cdot 2\text{H}_2\text{O}$ ($\text{A} = \text{NH}_2$ 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 complexes containing triply bonded peroxide (36).

The $^1$H NMR spectra of the monoperoxovanadium(V) complexes, [VO(O$_2$)$_2$QL], were recorded in DMSO-$d_6$ solvent. The significant features of the NMR spectra are the signals due to the coordinated 8-quinolinolate ligand and the coordinated L (L = EtOH, DMF, or THF). The signals due to coordinated 8-quinolinolate ligands, observed at $\delta$ 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 $\delta$ values 2.5(s), 3.6(m) -CH$_3$, and 2.83(s), respectively (39). The DMF signals, for L = DMF, were observed at $\delta$ 7.93(s), 2.83(s), and 2.7(s) assigned to HCO$^-$, -CH$_3$, and -OCH$_3$, respectively (ref. 39, p. 344). The THF signals of the corresponding complex appear at $\delta$ 1.73(m) and 3.6(m) due to -CH$_2$-CH$_2$- and -CH$_3$-O-CH$_2$-, respectively (ref. 39, p. 348). Thus, the $^1$H NMR results show conclusively that the 8-quinolinolate 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.

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