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Synthesis, Characterisation and Physicochemical Properties of Peroxo–Vanadium(V) Complexes with Glycine as the Hetero-ligand

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Abstract

The first glycine–peroxo complexes of vanadium-(V), $NH_4[VO(O_2)_2GlyH]\cdot H_2O$ (1), $K[VO(O_2)_2GlyH]\cdot H_2O$ (2) and $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$ (3) have been synthesised from the reaction of V_2O_5 with hydrogen peroxide and glycine (GlyH) at pH 3–4 (1 and 2) and pH 2 (3), respectively. The compounds have been characterised by elemental analysis, magnetic susceptibility and ESR, UV–Vis and IR spectroscopy. While glycine, occurring in its zwitterionic form, is coordinated to the V(V) centre in a monodentate fashion through its carboxylic oxygen, the peroxides in **1** and **2** occur as terminal bidentate ones. In compound **3** one of the peroxide ligands is present as a μ-peroxo group. Typically, an aqueous solution of **2** exhibits peroxo–V(V) LMCT bands at 328 and in the 200–190 nm region, whereas complex **3** shows only one broad LMCT band at 310–330 nm.

Introduction

Increasing interest in metal–amino acid [1–3] as well as peroxo–metal systems [4–9] mainly attributable to their potential as models for understanding biologically important molecules [1–10] prompted us to establish rational synthetic routes to peroxo–vanadium(V) complexes containing an amino acid as coligand. Vanadium has been identified as a bioessential metal [11–15], however, its actual biological function still remains an enigma [12, 15]. The recent discovery of vanadium containing enzymes, a bromoperoxidase [16] and a nitrogenase [17, 18], which contain vanadium(V), are considered to be major steps towards understanding the biochemistry of the metal. Moreover, peroxoheteroligand vanadium(V) complexes, besides being shown to be capable of oxidising organic substrates [4, 9, 10, 19], have been implicated to be actively involved in some biochemical processes [13, 20].

We considered that the coordination of an amino acid and a peroxide ligand at a vanadium(V) centre might lead to biochemically relevant systems, because all three constituents, viz. vanadium(V), peroxide and amino acid are of acknowledged biological significance. Besides, the possibility of such complexes exhibiting oxidising properties could not be ruled out. Pertinent here is to mention that, to the best of our knowledge peroxo–amino acid complexes of vanadium(V) have not been reported to exist in the solid state.

In this paper we describe the synthesis and structural assessment of two types of peroxo–glycine–vanadium(V) complexes, viz. $A[VO(O_2)_2GlyH]\cdot H_2O$ (A = NH_4 (1) and K (2)) and $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$ (3).

It was also of interest to develop peroxo heteroligand vanadate systems amenable to electronic spectroscopic studies. The study of electronic structures of the metal–dioxygen unit is of particular interest in relation to bonding of O_2 to the metal centres in metalloenzymes, oxygen carrying proteins, and also to catalytic oxidations. The compounds reported in this paper exhibit a rather typical electronic spectral pattern and provide an excellent scope for study of the peroxo–metal interactions in solution.

Experimental

The chemicals used were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Magnetic susceptibilities were measured by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant. The ESR spectra of the solids as well as those of aqueous solutions of the compounds were recorded using a Varian E109, X-band ESR spectrometer with 100 K_c field modulator. pH values of the reaction solutions were measured by using a Systronics Type 335 digital pH meter and also by pH indicator paper.

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Synthesis of Ammonium and Potassium Oxodiperoxoglycine Vanadate(V) Monohydrates, $A[VO(O_2)_2GlyH]\cdot H_2O$ ($A = NH_4$ (1) or K (2))

As the methods of synthesis of $A[VO(O_2)_2GlyH]\cdot H_2O$ compounds are similar, only a representative procedure is described.

Glycine (1.65 g, 21.97 mmol) was first dissolved in 30% hydrogen peroxide (20 cm^3, 176.3 mmol). To this was added V_2O_5 (1 g, 5.5 mmol) under constant stirring, maintaining the concentration ratio of V:glycine:H_2O_2 as 1:2:32. Before V_2O_5 was completely dissolved, a small amount of powdered potassium hydroxide or aqueous ammonia (sp. gr. 0.9) was added very carefully with stirring until the pH of the solution was adjusted to 3–4. A clear yellow solution was obtained at this stage. The reaction solution was stirred for a further period of *c.* 10 min to allow the reaction to be complete. The reaction was conducted at an ice-bath temperature. Addition of pre-cooled ethanol to the reaction solution obtained as above caused precipitation of a yellow oily mass which was separated by decantation. The separated mother liquor was treated repeatedly with ethanol to obtain another crop of the yellow oily product. The two lots of yellow oily mass thus obtained were combined together, treated repeatedly with acetone–ethanol (3:1, vol./vol.) mixture until it became solid. The solid alkali oxodiperoxoglycine vanadate(V) monohydrate $A[VO(O_2)_2GlyH]\cdot H_2O$ ($A = NH_4$ (1) or K (2)) was separated by centrifugation, washed with ethanol, and dried *in vacuo* over concentrated sulphuric acid.

Anal. Calc. for $NH_4[VO(O_2)_2GlyH]\cdot H_2O$: V, 21.07; O_2^{2-}, 26.44; C, 9.92; H, 4.54; N, 11.57. Found: V, 20.85; O_2^{2-}, 26.13; C, 10.04; H, 4.33; N, 11.92%. Calc. for $K[VO(O_2)_2GlyH]\cdot H_2O$: V, 19.39; O_2^{2-}, 24.33; C, 9.12; H, 2.66; N, 5.32. Found: V, 18.92; O_2^{2-}, 24.14; C, 9.26; H, 2.61; N, 5.93%.

Synthesis of $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$ (3)

A 1.0 g (5.5 mmol) sample of V_2O_5 was mixed with 0.83 g (11.06 mmol) of glycine (glyH), followed by a slow addition of 30% H_2O_2 (15 cm^3; 132.3 mmol) with stirring, maintaining the V:glycine:H_2O_2 ratio as 1:1:26. The reaction mixture was stirred for *c.* 15 min in an ice-bath keeping the temperature below 10 °C, whereupon a red solution resulted. To the above reaction solution was then added *c.* 50 cm^3 of acetone with continuous stirring. A saffron coloured pasty mass separated out at this stage. The reaction mixture was then cooled in a freezer for *c.* 1 h. The supernatant liquid was decanted off and the residue upon repeated treatment with acetone under scratching gave a microcystalline solid, which was filtered off, washed 3–4 times with actone, and finally dried *in vacuo* over concentrated H_2SO_4.

Anal. Calc. for $[V_2O_2(O_2)_3(glyH)_2(H_2O)_2]$: V, 24.49; O_2^{2-}, 23.08; C, 11.54; H, 3.40; N, 6.73. Found: V, 24.13; O_2^{2-}, 22.81; C, 11.23; H, 3.09; N, 6.25%.

Elemental Analyses

Vanadium, peroxide, and potassium were estimated by methods mentioned in our earlier papers [21, 22]. C, H and N analyses were performed by R.S.I.C., Central Drug Research Institute, Lucknow, India.

Results and Discussion

The reaction of vanadium with hydrogen peroxide is highly pH dependent, and a small variation of pH of the reaction solutions leads to formation of peroxo–vanadium complexes of varied compositions. The importance of pH, for the successful synthesis of peroxo–metal compounds has been emphasised in the literature [21, 23]. In the present case, it has been observed that slight variation of reaction conditions, viz. pH and order of addition of reactants leads to the formation of two types of peroxo–glycine compounds of vanadium(V). The suitable pH for bringing about coordination of both peroxo and glycine with the oxovanadate(V) centre leading to the synthesis of $A[VO(O_2)_2GlyH]\cdot H_2O$ complexes was ascertained to be 3–4, which was maintained by the addition of the corresponding alkali hydroxide. However, a similar reaction when conducted in the absence of alkali, at pH *c.* 2, yielded the molecular complex, $[V_2O_2(O_2)_3(GlyH)_2(H_2O)_2]$. It is also important to mention that the sequence of addition of the reactants is also an equally important parameter in order to achieve success in the synthesis of the two types of complexes described herein (see ‘Experimental’).

It may be inferred by considering the two types of reaction products, isolated from reaction solutions at different pH values, that during the synthesis of the complexes **1** and **2**, the bridged dimeric species **3** probably formed as an intermediate at pH 2, which then underwent decomposition with the addition of alkali leading to the formation of monomeric complexes **1** and **2** at pH 3–4. This explanation is in line with the proposition that with increasing pH of the reaction medium the number of peroxide groups bonded to the vanadium(V) centre increases [8].

The reactions were monitored by isolating a small amount of the product from the reaction solution and recording its IR spectrum. Appearance of a strong band at *c.* 860 cm^{-1} due to the ν(O–O) mode of the coordinated peroxide (O_2^{2-}), and the bands due to the occurrence of glycine indicate the formation of the complex species. Although synthesis could be achieved in the case of the NH_4^+ and K^+ salts of the complex $[VO(O_2)_2(GlyH)]^-$, attempts to synthesise the Na^+ salt of the complex ion have not been successful so far. An oily precipitate could be isolated in this case which did not permit solidification.

Complexes **1** and **2** are yellow microcrystalline products, hygroscopic in nature. Complex **3** is orange in colour and also highly hygroscopic. The compounds are soluble in water at ambient temperatures accompanied by slow decomposition. Unlike some other hetero-ligand peroxovanadate(V) compounds [21, 24], the peroxo vanadium(V) complexes containing glycine as the hetero-ligand are not very stable in the solid state for a prolonged period.

In an attempt to find out the possibility of removal of lattice water of complexes **1** and **2**, pyrolysis of the compounds was carried out at 100 °C. Unfortunately, the compounds started decomposing involving the simultaneous loss of both peroxide (O_2^{2-}) and H_2O, thus a genuine dehydration was not possible.

The peroxo–glycine–vanadate(V) compounds were diamagnetic in nature, as evident from the results of magnetic susceptibility measurements, in conformity with the occurrence of vanadium(V) in each of them. The compounds were also ESR silent. The peroxide estimation results conspicuously suggested the presence of two peroxides per vanadium(V) centre in compounds **1** and **2**, whereas the O_2^{2-}:V ratio was found to be 3:2 in the case of complex **3**. This suggested a dimeric nature for complex **3** presumably involving a bridging peroxide ligand.

It was hoped to develop peroxo–vanadium(V) systems suitable for electronic spectral probes in the studies of metal–dioxygen bonding. It is relevant to mention that recording of electronic spectra is not always successful in the case of peroxo–metal complexes [2]. In a typical case of a metal complex containing peroxides as a terminal ligand, two peroxo (LMCT) bands are expected in its electronic spectra due to two types of transitions [25, 26] viz. $\pi^*_v \rightarrow d\sigma^*$ and $(\sigma)\pi^*_v \rightarrow d\sigma^*$. The latter transition which involves much higher energy, has rarely been identified [25, 26] in the spectra of most of the peroxo complexes. In the case of a bridging peroxide, however, a single (LMCT) band is expected in the visible region due to the $\pi^* \rightarrow d$ transition [25, 26]. Fortunately, the newly synthesised complex **2** enabled us to observe both the predicted transitions. The peroxo (LMCT) bands of the complex $K[VO(O_2)_2GlyH]\cdot H_2O$ have been clearly resolved in aqueous solutions at 328 and 200–190 nm, respectively. The peroxo–metal charge transfer band at 328 nm of weak intensity ($\epsilon = 7 \times 10^2$) has been assigned at the $\pi^*_v \rightarrow d\sigma^*$ transition. The broad band as observed in the 200–190 nm region, with the molar absorption $\epsilon = 1 \times 10^4$, is especially significant because this particular transition is not generally observed in most cases of peroxo–metallates. This absorption is assigned to the $(\sigma)\pi^*_v \rightarrow d\sigma^*$ transition [25, 26]. The spectrum of complex **3** contains a single broad LMCT band in the 310–330 nm ($\epsilon = 1.3 \times 10^2$) region. No other bands attributable to transitions involving dioxygen were observed in the examined region (180–800 nm).

The significant features of the IR spectra of complexes **1**, **2** and **3** involve absorptions due to ν(V=O), coordinated peroxide, coordinated glycine, and coordinated as well as lattice water. The strong band at *c.* 960 cm^{-1} has been assigned to ν(V=O) arising from the terminally bonded V=O group. From previous experience of dealing with IR spectra of various kinds of peroxo–element species [21, 27, 28] the bands at *c.* 850, *c.* 605, *c.* 510 cm^{-1} have been assigned to the coordinated peroxide groups. This observance is rather typical of the O_2^{2-} ligand, bonded to the metal centre in a triangular bidentate (C_{2v}) manner. However, in the molecular dimeric complex **3** the ν(O–O) mode was observed at a slightly lower range, i.e. at 820 cm^{-1}, which is also broadened. This may be due to the combination of the ν(O–O) vibrations of the peroxide groups bonded to the vanadium(V) centre in two different fashions, viz. bridging as well as terminal.

Amino acids are known to form complexes with metals in either the neutral zwitterionic form or in the anionic form, of which the latter form is most common among the published monomeric solid structures. In the present case the frequencies observed at *c.* 1640s, *c.* 1395s, *c.* 1120m, *c.* 690m, and *c.* 595 cm^{-1} are due to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, $\varphi_r(NH_3^+)$, $\varphi_w(COO^-)$ and $\delta(COO^-)$ modes, respectively, of the coordinated glycine [1, 29a]. Notably important in this context are (i) increase in $\nu_{as}(COO^-)$, (ii) decrease of $\nu_s(COO^-)$, and (iii) unaltered positions of N–H stretching frequencies as compared to an uncoordinated glycine. The observations in the present case suggest that glycine in compounds **1**, **2** and **3** occurs in its zwitterionic form ($NH_3^+CH_2COO^-$), and is bonded to the metal centre through its carboxylic oxygen. Thus, although glycine can act as a bidentate ligand, in the present case it appears that this ligand acts as a monodentate one being bonded in the fashion described above. This kind of bonding of glycine via oxygen, and their coordination as zwitterions, which is an interesting structural feature in these complexes, is not very common, but has been reported previously [1, 2].

Another notable feature of the IR spectra of complexes **1** and **2** is that two additional bands have been observed at *c.* 1658 and *c.* 3410 cm^{-1}, which resemble in their shapes and positions those commonly observed for uncoordinated water and have been accordingly assigned to the δ(H–O–H) and ν(O–H) modes, respectively. The region in which the ν(O–H) band has been observed in the present case is rather typical of lattice water [30]. However, in the case of complex **3**, in addition to the observance of δ(H–O–H) and ν(O–H) at *c.* 1650 and *c.* 3400 cm^{-1}, respectively, another medium intensity band appears at *c.* 740 cm^{-1} which has been assigned to the rocking mode of coordinated water [29b]. This observation clearly suggests that the water molecules in the latter complex are coordinated to the metal centre.

Conclusions

It has been shown that it is possible to bring about coordination of glycine in the presence of peroxide to a vanadium(V) centre under appropriate experimental conditions. The synthesis of two types of complexes, viz. $A[VO(O_2)_2GlyH]\cdot H_2O$ and $[V_2O_2(O_2)_3GlyH)_2(H_2O)_2]$ can be achieved by reacting V_2O_5 and glycine directly with H_2O_2 with a small variation of pH of the medium and making a change in the order of addition of the reactants. The pattern of the IR spectra renders it certain that the glycine ligand binds the vanadium(V) centre as zwitterions via the carboxylic oxygen. The peroxo LMCT bands are well resolved in the complexes.

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