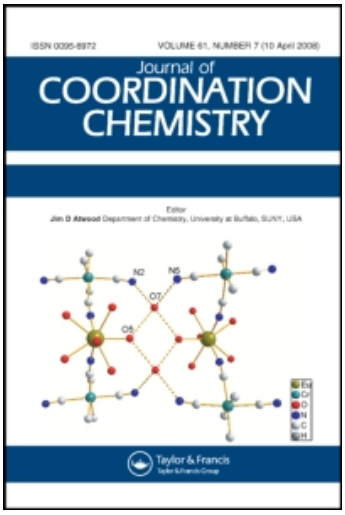

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND CHARACTERIZATION OF NEW OXODIPEROXOVANADATE COMPLEXES CONTAINING COORDINATED AMINOACIDS

A. E. Gerbase[a]; M. Martinelli[a]; L. G. Fagundes[a]; V. Stefani[a]; S. J. Da Silva[a]
[a] Instituto de Quimica, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS. Brazil

To cite this Article Gerbase, A. E. , Martinelli, M. , Fagundes, L. G. , Stefani, V. and Silva, S. J. Da(1999) 'SYNTHESIS AND CHARACTERIZATION OF NEW OXODIPEROXOVANADATE COMPLEXES CONTAINING COORDINATED AMINOACIDS', Journal of Coordination Chemistry, 47: 3, 451 — 458
To link to this Article: DOI: 10.1080/00958979908022230
URL: http://dx.doi.org/10.1080/00958979908022230

J. Coord. Chem., 1999, Vol. 47, pp. 451–458
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND CHARACTERIZATION OF NEW OXODIPEROXOVANADATE COMPLEXES CONTAINING COORDINATED AMINOACIDS

A.E. GERBASE*, M. MARTINELLI, L.G. FAGUNDES, V. STEFANI and S.J. DA SILVA

Instituto de Química, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil

(Received 27 October 1997; Revised 31 March 1998; In final form 22 September 1998)

The study of peroxovanadium compounds has received renewed attention since the discovery of their insulin mimetic properties and of the vanadium bromoperoxidase enzyme which catalyzes the oxidation of halides by hydrogen peroxide. This work presents the synthesis and characterization of three novel oxodiperoxovanadium complexes, $K_n[VO(O_2)_2AA] \cdot 2H_2O$, where AA = L-asparagine(**1**), L-phenylglycine(**2**), D,L-homocystine(**3**). The products were synthesized by the reaction of V_2O_5, with the amino acid and H_2O_2 at room temperature. The compounds obtained are yellow, soluble in water and insoluble in organic solvents. They show remarkable hygroscopic character and are light and temperature sensitive. IR and UV-VIS spectra of the compounds show the typical oxo and diperoxo bands ($\nu_{V=O} = 970\,cm^{-1}$, $\nu_{VO-O} = 870\,cm^{-1}$, $\nu_{V-O_2} = 630$, $525\,cm^{-1}$, $\lambda \cong 320\,nm$). The ligand bonding properties were determined on the basis of electric conductivity and spectroscopic data (IR, ^1H NMR) as well as elemental analysis.

Keywords: Vanadium; peroxo compounds; amino acids

INTRODUCTION

The coordination chemistry of peroxovanadates has had a renewed interest in recent years since bromo and iodo peroxidase vanadium-based enzymes

* Corresponding author. Tel.: (+)55 51 316 6259. Fax: (+)55 51 319 1499.
E-mail: agerbase@vortex.ufrgs.br.

were discovered in marine algae, and the insulin mimetic properties of peroxovanadium complexes were reported.[1–4] Peroxovanadates are known as catalysts of several oxidation reactions, alkene and allylic alcohol epoxidation or hydroxylation, sulfide oxidation and arene and alkane hydroxylation.[5–7] A great number of peroxovanadium complexes have been synthesized,[1,4,8–16] their crystal structures determined, and their behavior in solution studied.[8,9] Their reactivity and oxidative ability are closely related to the nature of the ligands present in the vanadium complexes.

In this context, peroxo complexes containing bio-heteroligands, such as amino acids, represent an interesting class of complexes.[15] There are numerous examples of the *in vivo* interaction of transition metal ions with amino acids and peptides, and these interactions are of considerable biological importance. These ligands, essential to life, exist as *zwitterions*, in the solid state, but almost invariably coordinate as anionic species. Depending upon the pH of the solution, the amino acids can coordinate to the metal through either or both the amino (NH_2) or carboxylate (COO^-) groups in aqueous media. The most usual mode of coordination is the bidentate chelate through the N and O atoms, which gives rise to a thermodynamically stable five-membered ring for the α-amino acids.[17,18] Monodentate coordination through the N atom has been established for some inert metal ions like Cr^{III}, Co^{III}, Ir^{III}, Rh^{III}. Monocoordination through the O atom is not so common.[18,19]

In this work we describe the synthesis and discuss the spectroscopic characterization of the novel oxodiperoxovanadium complexes with non-coordinating side chain amino acids, such as L-phenylglycine, and with coordinating side chain amino acids, such as L-asparagine, D,L-homocystine.

EXPERIMENTAL

General Procedures and Analyses

All manipulations were carried out in air, and a hood with a protective shield was used as sometimes unexpectedly violent reactions can occur. V_2O_5 (99%, Merck), H_2O_2 (30 w/v, Merck), KOH (99%, Merck), L-asparagine, D,L-homocystine and L-phenylglycine were used without purification. Elemental analyses were performed on a Perkin-Elmer 2400-CHN apparatus. V and K were determined by atomic absorption spectroscopy using a Hitachi Z8230 apparatus. Molar electrical conductivity measurements of the aqueous solutions were carried out on a Digimed CD 21 apparatus using standard solutions for calibration.

Infrared spectra were recorded as KBr disks on a Mattson Galaxy Series FTIR 3000 spectrophotometer. UV-VIS spectra were obtained on a Shimadzu spectrophotometer UV-160, in quartz cuvettes with 1 cm of optical pathway. ^{1}H NMR spectra were obtained on a Varian VXR 200 spectrometer operating at 200 MHz at room temperature, using D_2O as solvent. All chemical shifts are in ppm relative to TMS using the positive downfield convention.

Syntheses

Preparation of $K[VO(O_2)_2AsnH] \cdot 2H_2O$ (1)

V_2O_5 (730 mg, 4 mmol) was dissolved in water (80 mL) with the addition of KOH until pH = 7 was reached. The clear yellowish solution was cooled in ice and H_2O_2 (30%, 8 mL, 70 mmol) was added dropwise with stirring. When it reached room temperature L-asparagine (1.20 g, 8 mmol) was added. The reacting mixture (pH = 5) was stirred at room temperature until all the amino acid had reacted. The solution was concentrated and ethanol was added until turbidity. The product was left at 10°C for some hours, then the precipitate was filtered, washed with cold water, cold ethanol and dried over vacuum (10^{-2} torr). The orange product was soluble in water and highly hygroscopic. Yield: 75%. Anal. Calcd. for $C_4H_{11}KN_2O_{10}V$ (%): C, 14.25; H, 3.26; K, 11.57; N, 8.31; V, 15.13. Found: C, 14.06; H, 3.36; K, 11.82; N, 8.27; V, 15.39.

Preparation of $K_2[VO(O_2)_2PheGly] \cdot 2H_2O$ (2)

This complex was prepared by the same procedure as above using V_2O_5 (730 mg, 4 mmol), H_2O_2 (30%, 8 mL, 70 mmol), L-phenylglycine (1.21 g, 8 mmol). Yield: 75%.

Preparation of $K_4[O\{VO(O_2)_2\}_2HomoCys] \cdot 2H_2O$ (3)

This complex was prepared by the same procedure as above using V_2O_5 (730 mg, 4 mmol), H_2O_2 (30%, 8 mL, 70 mmol), D,L-homocystine (2.14 g, 8 mmol). Yield: 62%. Anal. Calcd. for $C_8H_{18}K_4N_2O_{19}S_2V_2$ (%): C, 12.50; H, 2.34; K, 20.31; N, 3.65; V, 13.28. Found: C, 11.02; H, 2.36; K, 19.72; N, 3.57; V, 12.77.

RESULTS AND DISCUSSION

The complexes were obtained from the reaction of V_2O_5, KOH, H_2O_2 and the respective amino acid in aqueous solution at room temperature.

The reaction of V_2O_5 and H_2O_2 is highly pH dependent and a small variation of the pH of the reaction solution leads to the formation of peroxovanadate complexes of different compositions. The number of peroxy groups coordinated to the metal increases as the pH of the solution is raised. Similarly, the mode of coordination of the amino acids varies with pH. The pH values of the reactions solutions were fixed at 5 when the amino acid was added. At this pH all the amino acids studied have a *zwitterion* character.

The compounds obtained are yellow in color. They are not very stable at room temperature in the solid state and decompose gradually by losing peroxides, changing from yellow to dark green. Loss of peroxide leads to reduction from V(V) to V(IV). We were not successful in getting large and pure crystals for X-ray structure analysis. On trying the recrystallization, from water or hydrogen peroxide solutions, partially decomposed products were produced. This problem also caused the poor elemental analyses obtained for compounds **2** and **3**.

Syntheses of peroxovanadates complexes are not always reproducible since they are sensitive to the concentration of metal and ligands, the temperature, the pH, and the reagent addition sequence. The basic problem is coprecipitation of either oxoperoxovanadates that do not contain the ligand or an excess of heteroligand. This behavior is associated with the nature of the heteroligand and was also observed in other peroxocomplexes.[1,20–23]

The complexes are highly soluble in water and insoluble in normal organic solvents. The electronic spectra of aqueous solutions of the complexes show two peroxo → vanadium charge transfer bands at *ca.* 325 nm ($\varepsilon \approx 500\ L\ mol^{-1}\ cm^{-1}$) and at *ca.* 220 nm ($\varepsilon \approx 10^4\ L\ mol^{-1}\ cm^{-1}$). The values obtained are presented in Table I. These two bands are expected in the case of metal complexes containing two terminal bidentate peroxide ligands.[1,22,23]

^1H NMR spectra were obtained in D_2O, and the data concerning the free amino acids and their complexes are presented in Table I. They confirm the

TABLE I ^1H NMR and UV/VIS data for the free amino acids and their complexes

Compound	δ (ppm)			λ_{max}(nm)/ε(L mol^{-1} cm^{-1})
	α-CH	*β-CH₂*	*γ-CH₂*	
L-asparagine	3.94 (m)	2.84 (d)		—
1	4.05 (s, br)	2.93 (s, br)		327 (920)
L-phenylglycine	4.4	7.4		—
2	4.7	7.4		330 (600)
D,L- homocystine*	—	—	—	—
3	3.67 (1H, t)	2.80 (2H, m)	2.09 (2H, m)	335 (2100)

*Insoluble in the available deuterated solvents.

IR evidence regarding coordination of amino acids, the resonance of the α-CH proton rapidly broadens and shifts to lower field. These shifts are very small but on the same order as analogous vanadium and molybdenum compounds with nicotinic acid.[8] The broadening of the signals is caused by partial decomposition and hydrolysis in water, but it is still possible to measure the chemical shifts, and in some cases the spin–spin coupling constant.

The IR spectroscopy is a very powerful tool for the characterization of peroxovanadate complexes since it gives information about coordination of the peroxo and ligand groups when compared with spectra of the free ligand. The IR data for the free amino acids dealt with in this work and their complexes are listed in Table II.

The strong and broad absorption in the 3500–3300 cm^{-1} range reflects the presence of a hydrogen bonded water network in the complexes. Complexation through the carboxyl group removes the *zwitterion* character, as can be seen by the absence of bands in the region 3100–2900 cm^{-1} corresponding to the NH_3^+ stretching, and by the presence of the normal NH_2 absorptions of a coordinated primary amine near 3250 cm^{-1} in the spectra of the complexes.[24,25]

When the amino acids coordinate to vanadium, the $\nu_{as}COO^-$ and ν_sCOO^- separation increases, which is an indication of monodentate complexation through the carboxylate group.[26,27] In complexes **2** and **3** the $\nu_{as}COO^-$ shifts to higher frequencies in relation to the free ligand, and the ν_sCOO^- absorption remains almost the same. This result indicates that phenylglycine and homocystine are bonded to the metal through the carboxylate group. On the other hand, in complex **1**, the mode of coordination is not evident. In this complex the $\nu_{as}COO^-$ remains almost in the same as the free ligand. The unaltered position of $\nu_{as}COO^-$ at 1638 cm^{-1} shows that the carboxylate group is not coordinated to the metal center.

TABLE II Relevant IR data for compounds **1–3** in comparison with those of the free amino acids (cm^{-1})

Asn	**1**	*PheGly*	**2**	*HomoCys*	**3**	*Assignt*
—	3410 br	—	3430 br	—	3450 s,br	νOH
3450, 3382	3184 br	—	3220 br	—	3240 br	νNH_2
3112, 2940	—	3100–2800	—	3050 br	—	νNH_3^+
1528 s	—	1510 s	—	1572 sh	—	$\delta_s NH_3^+$
1643 vs	1638 vs,br	1611 s,br	1658 vs,br	1601 s,br	1644 vs, br	$\nu_{as}COO^-$
1431 s	1401 s	1397 s	1404 s	1411 s	1410 s	ν_sCOO^-
—	968 s	—	965 s	—	964 s	νV=O
—	871 m	—	869	—	872 m	νO–O
—	630	—	630	—	615 s	$\nu_{as}M(O_2)$
—	527	—	520 sh	—	530 sh	$\nu_sM(O_2)$

The IR spectra of the complexes show the characteristic V=O strong stretching band at 970 cm^{-1} as well as the typical bands of bidentate peroxy groups, $\nu O-O$, $\nu_{as}M(O_2)$, $\nu_sM(O_2)$.[28] The O–O stretching frequencies for oxodiperoxo complexes appear as a strong band near 880 cm^{-1} whereas in monoperoxo complexes this band occurs around 930 cm^{-1}. In complexes **1**, **2** and **3**, we observe the presence of a strong band at 870 cm^{-1} which indicates the formation of diperoxo complexes. This is in agreement with the UV-VIS data described before.

Important structural distinctions can be determined from the asymmetric and symmetric metal-peroxo vibrations, $\nu_{as}M(O_2)$, $\nu_sM(O_2)$. On a diperoxo complex with a monodentate ligand, which corresponds to a pentagonal pyramidal symmetry, a splitting of roughly 100 cm^{-1} is observed, with the bands occurring approximately at 630 and 520 cm^{-1}. If the spectrum shows a splitting of roughly 40 cm^{-1}, with two bands occurring at approximately 625 and 585 cm^{-1}, it is an indication of a bidentate ligand with a pentagonal bipyramidal complex.[5] The band separations in our complexes are in the range of 85–110 cm^{-1}, which suggests the formation of a diperoxocomplex with a monodentate ligand. This is in agreement with Tracey and Jaswal,[29] who studied the reaction between mono and diperoxovanadate and a number of amino acids by ^1H and ^{51}V NMR. They found that in the monoperoxo complexes the amino acid coordinates in a bidentate form but in diperoxovanadium compounds bidentate complexation of amino acids was not observed. Complexation occurred through either the carboxyl or the amino groups, with coordination of the amino position favored.

Conductivity measurements obtained for aqueous solutions of complexes **1**, **2** and **3** are typical of electrolyte compounds. Compound **1** has a smaller conductivity of 115 $S\,mol^{-1}\,cm^2$, which confirms its 1 : 1 electrolyte nature. Complex **2** has a value of 248 $S\,mol^{-1}\,cm^2$, in accordance with a 2 : 1 electrolyte. This result indicates that in this complex the L-phenylglycine behaves as an anionic ligand. For complex **3** we obtain the highest value, 481 $S\,mol^{-1}\,cm^2$, corresponding to 4 : 1 electrolyte. These data suggest that the amino acids are bonded in different ways in the complexes. In complex **1** it binds in a neutral form as observed for the analogous glycine compound[22] whereas in compounds **2** and **3** they coordinate as anionic species through the O atom.

The spectroscopic data show that the amino acids used in this work can be employed to prepare peroxovanadium complexes. The first amino acid, L-asparagine, coordinates to the vanadium atom in the neutral form AsnH probably through the N of the amino group. Despite the fact that this amino acid has a coordinating side chain, no evidence shows chelation

occurring through the N(amide). In fact the IR data indicate the presence of a monodentate ligand. The coordination of two peroxy groups was evidenced by UV/VIS and IR.

In the case of compound **2** the reaction is extremely slow because of the partial insolubility of L-phenylglycine in aqueous media. As the amino acid is consumed the reaction proceeds. Formation of the oxodiperoxo complex is shown by spectroscopic data and the molar conductivity; it is clear by IR spectroscopy that L-phenylglycine coordinates to the vanadium metal as a monodentate anionic ligand through the O atom. The poor elemental analysis observed for this compound can be caused by its highly hygroscopic nature and/or its instability in the solid state. Indeed this compound was the most unstable of the series.

Finally, when we use the D,L-homocystine amino acid in compound **3**, the spectroscopic data, as well as the electrical conductivity and the elemental analysis, show that this ligand bridges two oxodiperoxovanadium moieties through each of its carboxylate groups. There is no evidence of a coordination through the sulfur atom. The same coordination was observed when the analog aminoacid, cystine, was prepared.[1]

In conclusion, in this work we synthesized and characterized three new oxoperoxovanadate complexes with amino acids. The amino acids used were L-asparagine, L-phenylglycine and D,L-homocistine. The first coordinates to the vanadium atom in a neutral form, but the last two do as anionic ligands. All the complexes present one oxo ligand, two peroxo anions, and one monodentate amino acid ligand in the inner coordination sphere of vanadium. There is no evidence that the amino acids with coordinating side chain use the extra site to form a complex .The compounds synthesized are electrolyte species, highly soluble in water. They show a remarkable hygroscopic character and are light and temperature sensitive. Decomposition by losing the peroxy ligands makes the V(V) oxidation state unstable, and leads to the reduction from V(V) to V(IV), with the subsequent change in color from yellow to dark green.

Acknowledgement

We thank the CNPq for award of research fellowship and financial support.

References

[1] C. Djordjevic, N. Vuletic, M.L. Renslo, B.C. Puryear and R. Alimard, *Mol. Cell. Biochem.* **153**, 25 (1995).

[2] C. Orvig, K.H. Thompson, M. Batell and J.H. McNeill, *Metals Ions in Biological Systems: Vanadium and its Role in Life*. (Marcel Dekker Inc., New York, 1995), Chapter 17, Vanadium Compounds as Insulin Mimics. p. 575.
[3] C. Djordjevic, *Metals ions in Biological Systems: Vanadium and Its Role in Life*. (Marcel Dekker Inc., New York, 1995), Chapter 18, Antitumor Activity of Vanadium Compounds, p. 595
[4] B.I. Posner, R.F. Faure, J.W. Burgess, A.P. Bevan, D. Lachance, G. Zhang-Sun, I.G. Fantus, J.B. Ng, D.A. Hall, B. Soo Lum *et al.*, *J. Biol. Chem.* **269**, 4596 (1994).
[5] A. Butler, M.J. Clague and G.E. Meister, *Chem. Rev.* **94**, 625 (1994).
[6] K.A. Jorgensen, *Chem. Rev.* **89**, 431 (1989).
[7] C.K. Sams and K.A. Jorgensen, *Acta Chem. Scand. A* **49**, 839 (1995).
[8] C. Djordjevic, B.C. Puryear, N. Vuletic, C.J. Abelt and S.J. Sheffield, *Inorg. Chem.* **27**, 2926 (1988).
[9] A. Shaver, D. Hall, B.S. Lum, B. Posner, J.B. Ng, *Inorg. Chem.* **32**, 3109 (1993).
[10] K. Wieghardt and U. Quilitzsch, *Inorg. Chem.* **18**, 869 (1979).
[11] R.E. Drew and F.W.B. Einstein, *Inorg. Chem.* **11**, 1079 (1972).
[12] N. Vuletic and C. Djordjevic, *J. Chem. Soc. Dalton Trans.* 1137 (1973).
[13] C. Djordjevic, M. Lee and E. Sinn, *Inorg. Chem.* **28**, 719 (1989).
[14] C. Djordjevic, P.L. Wilkins, E. Sinn and R.J. Butcher, *Inorg. Chim. Acta* **230**, 241 (1995).
[15] C. Djordjevic, M.L. Renslo and E. Sinn, *Inorg. Chim. Acta* **233**, 97 (1995).
[16] F.W.B. Einstein, R.J. Btchelor, S.J. Angus-Dunne and A. Tracey, *Inorg. Chem.* **36**, 1680 (1996).
[17] K. Nakamoto, Y. Morito and A.E. Martell, *J. Am. Chem. Soc.* **83**, 4528 (1961).
[18] S.H. Laurie and G. Wilkinson, *Comprehensive Coordination Chemistry, The Synthesis, Reactions, Properties and Applications* (Pergamon Press, Oxford, 1987); Vol. 2, Chapter 20: Amino Acids, Peptides and Proteins, p. 739.
[19] C.A. McAuliffe and W.D. Perry, *J. Chem. Soc.* (*A*) 634 (1969).
[20] H. Mimoun, L. Saussine, E. Daire, M. Postel, D. Fischer and R. Weiss, *J. Am. Chem. Soc.* **105**, 3101 (1983).
[21] M. Bonchio, V. Conte, F. Di Furia, G. Modena and S. Moro, *Inorg. Chem.* **33**, 1631 (1994).
[22] M. Bhattarcharjee, M.K. Chaudhuri, N.S. Islam and P.C. Paul, *Inorg. Chim. Acta* **169**, 97 (1990).
[23] J. Mukherjee and M. Bhattarcharjee, *Indian J. Chem. A* **35**, 471 (1996).
[24] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. (Wiley & Sons, 3rd ed., 1978), p. 305.
[25] L.J. Bellamy, *The Infrared Spectra of Complex Molecules* (Chapman and Hall, 3rd ed, London, 1976), Vol. 2, p. 263.
[26] S.T. Chow and C.A. McAuliffe, *Prog. Inorg. Chem.* **19**, 51 (1975).
[27] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
[28] N.J. Campbell, W.P. Griffith and A.C. Dengel, *Polyhedron* **8**, 1379 (1989).
[29] A. Tracey and J.S. Jaswal, *Inorg. Chem.* **32**, 4235 (1993).