Fluoride-assisted stabilisation of amino acid complexes of vanadium Synthesis and characterisation

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Abstract

Fluoride amino acid complexes of vanadium(IV) of the type $A[VOF_2L(H_2O)]$ (A = Na or NH_4, L = cysteinate) and $A[VOF_3L(H_2O)]$ (A = NH_4 for L = alanine and A = Na, NH_4 or K for L = serine) have been synthesised. The compounds have been characterised by chemical analyses, chemical determination of the oxidation state of vanadium, solution electrical conductance and magnetic susceptibility measurements, ESR, IR and electronic spectral studies. The vibrational spectra of the complexes indicate coordination of the amino acids through their carboxylate group to the metal centre. Also, the sulphydryl functionality provides an additional coordination site in cysteine-containing complexes. Fluoride appears to act as a stabilising ligand which helps in the solid-state isolation of the complexes.

Keywords: Fluoride-assisted stabilisation; Amino acid complexes; Vanadium; Synthesis; ESR spectroscopy; IR spectroscopy; Magnetic susceptibility; UV spectroscopy

1. Introduction

Earlier studies on metal–amino acid interaction [1,2] led to the development of amino acid complexes of metals like copper, lead, mercury, cadmium, etc. [2–4], thereby providing an insight into the potential use of complexes with ligands as therapeutic agents. Studies on the interaction of vanadium with amino acids gained momentum after the recognition that the metal is of biochemical relevance. However, a literature survey has revealed that very few data exist that may be used to understand such interactions [5]. A number of reports, including some very recent ones, have been concerned with vanadium–amino acid systems in solution from which the isolation of the pure compound was not possible [6]. Only in a few cases has the isolation of solids been claimed, and the information available still seems to be inadequate [5,7]. In addition, very few oxovanadium complexes with S and N donor atoms have been isolated from solution and characterised [8]. No vanadium(IV) complexes with cysteine have been isolated as solids although a complex of vanadium(IV) with cysteine methyl ester is known [8,9]. The paucity of information in the vanadium–amino acid system appears to be due in part to the absence of a synthetic route to such

complexes. Furthermore, solution studies involving VO^{2+} and N-donor ligands have revealed that in order to achieve an appropriate free ligand concentration for complex formation, the reactions must be conducted at a relatively high pH. But at pH > 4, the tendency for hydrolysis of the VO^{2+} ion is appreciable and the nature of the products obtained is not well understood [5].

In view of the above, the development of a suitable synthetic route to these systems was considered necessary. In order to achieve such synthesis, the use of fluoride was considered suitable in the hope that it might help stabilisation and hence isolation of the compounds in the solid state. Fluoride and oxide ligands are known to stabilise high oxidation states, i.e. +4 and +5 of vanadium [10–12]. Accordingly, reactions were conducted in the presence of fluorinating agents such as AHF_2 (A = Na, NH_4 or K), aqueous HF or a combination of aqueous HF and NH_4F, all of which also helped in maintaining the pH of the reaction medium at ca. 4 which in turn might prevent hydrolysis of the VO^{2+} ion. In the present case, reduction of vanadium(V) to vanadium(IV) was achieved by using a sacrificial reductant, i.e. hydrazine hydrate, to obtain the alanine and serine complexes, whereas cysteine itself acted as a reductant for the cysteine complexes. However, our attempts to prepare fluorovanadium(V) complexes of the amino acids have not been successful.

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2. Experimental details

Reagent grade chemicals were used for the syntheses. Fresh samples of AHF_2 (A = Na, NH_4 or K) were prepared by the method described earlier [13]. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer as KBr pellets. ESR spectra were obtained at ambient temperature on a Varian E-109 spectrometer (X-band) with 100 kHz field modulation. Magnetic susceptibility measurements were made by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra were recorded on a Hitachi model 330 spectrophotometer. The pH of the reaction solutions were measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper. Vanadium, fluoride, sodium and potassium, and carbon, hydrogen and nitrogen, were all analysed as reported earlier [14–16].

2.1. Synthesis of $A[VOF_2(CysH)(H_2O)]$ (A = Na or NH_4)

A representative procedure for the synthesis of $NH_4[VOF_2(CysH)(H_2O)]$ is described as an example. An aqueous suspension (15–20 cm^3) of 0.5 g (4.27 mmol) of NH_4VO_3 was placed in a polyethylene beaker and dissolved in 1 cm^3 (23.99 mmol) of 48% hydrofluoric acid by heating on a steam bath. To the clear solution, was added 1.5 g (8.54 mmol) of solid L-cysteine hydrochloride monohydrate. As soon as the solid cysteine hydrochloride monohydrate was added, the pale yellow solution changed colour to blue due to reduction of vanadium(V) to vanadium(IV) with concomitant precipitation of cysteine. The whole was heated on a steam bath for 5–10 min to allow complete precipitation of cysteine which was filtered out. The filtrate was then concentrated to a blue oily mass at steam bath temperature. The oil thus obtained was washed four or five times with 5–10 cm^3 portions of ethanol followed by scratching on against the walls of the reaction container to obtain the blue solid $NH_4[VOF_2(CysH)(H_2O)]$. The solid was filtered out and dried in vacuo over conc. H_2SO_4.

The synthesis of $Na[VOF_2(CysH)(H_2O]$ was achieved from 0.5 g (4.10 mmol) of $NaVO_3$, 1 cm^3 (23.99 mmol) of 48% HF and 1.44 g (8.20 mmol) of L-cysteine hydrochloride monohydrate. The compound $NH_4[VOF_2(CysH)(H_2O)]$ could also be obtained in 65% yield by dissolving an aqueous suspension (15–20 cm^3) of 0.5 g (2.75 mmol) of V_2O_5 in a solution of 1 cm^3 (23.99 mmol) of 48% HF containing 0.31 g (8.37 mmol) of NH_4F, followed by interaction with 0.97 g (5.52 mmol) of L-cysteine hydrochloride monohydrate.

2.2. Synthesis of $A[VOF_3L(H_2O)]$ (A = NH_4 for L = L-alanine and A = Na, NH_4 or K for L = L-serine)

An aqueous suspension (15–20 cm^3) of 0.5 g (2.75 mmol) of V_2O_5 was treated with 0.55 g (9.64 mmol) of NH_4HF_2 or 0.75 g (9.60 mmol) of KHF_2 or 0.60 g (9.68 mmol) of $NaHF_2$ followed by heating on a steam bath to obtain a clear

solution. Solid amino acid, 0.49 g (5.50 mmol) of L-alanine or 0.58 g (5.52 mmol) of L-serine, was then added to the solution. The dissolved vanadium(V) was reduced by dropwise addition of hydrazine monohydrate until the pale yellow colour of the solution changed to deep blue. The solution was concentrated to a blue oil at steam bath temperature. The oil thus obtained was washed four or five times with ethanol followed by scratching on the walls of the container to obtain blue and bluish-violet $A[VOF_3L(H_2O)]$. The compound was isolated by filtration and dried in vacuo over conc. H_2SO_4.

3. Results and discussion

The ability of cysteine to act as a reducing agent [17] as well as a ligand allowed the successful synthesis of fluorocysteinate complexes of VO^{2+} from the reaction of VO_3^- and L-cysteine at a 1:2 molar ratio in the presence of hydrofluoric acid.

The blue $A[VOF_2(CysH)(H_2O)]$ (A = Na or NH_4) materials were characterised by a combination of elemental analyses, magnetic moment measurements, IR, EPR and electronic spectral studies. The IR spectral analysis provided significant information for characterisation of the compounds (Table 1). The $\nu(V=O)$ peak was observed at ca. 980 cm^{-1}, while the sharp band at 520 (s) cm^{-1} was attributed to $\nu(V-F)$ [18]. The $\nu(V-O)$ and $\nu(V-S)$ modes generally occur at relatively lower frequencies. The appearance of $\rho_r(H_2O)$ at ca. 745 (m) cm^{-1}, in addition to the $\nu(O-H)$ and $\delta(H-O-H)$ modes at ca. 3420 (m) and ca. 1625 (s, br) cm^{-1}, respectively, provides clear evidence for the presence of coordinated water. The broadening of the $\delta(H-O-H)$ mode for water is due to its overlap with the ν_{as} mode of the COO^- group of the amino acid. The presence of the symmetric deformation mode of NH_3^+ at 1484 and 1507 cm^{-1} for the ammonium and sodium salts, respectively, of the complex ruled out coordination through nitrogen [19,20]. The NH_3^+ stretching region at ca. 3430 cm^{-1} was obscured to some extent owing to the presence of coordinated water. The shift in the ν_{as} mode of COO^- to a higher frequency (ca. 1625 (s) cm^{-1}) and the ν_s mode of COO^- to a lower frequency (ca. 1390 (s) cm^{-1}) in comparison to those in the free cysteine moiety [20] suggested coordination through an O atom of the COO^- group in a unidentate [20] fashion. This was further complemented by the appearance of a $\nu(V-O)$ band at ca. 475 (m) cm^{-1}. The absence of any band at ca. 2565 cm^{-1} suggested deprotonation of the sulphydryl group [20]. This, coupled with the $\nu(V-S)$ mode observed at 370 (s) cm^{-1}, suggested additional coordination through the S atom of cysteine to the metal centre. Besides these, the ammonium salt of the complex exhibited a strong band at 1427 cm^{-1} which was assigned to the $[\nu(N-H)\nu_4]$ mode of the NH_4^+ ion. The IR spectra of the complexes thus clearly indicate the presence of V=O, V–F, coordinated water and the occurrence of the cysteinate ligand as a chelated

Table 1
Important IR and electronic spectral bands for the complexes studied

Compound	IR (cm^{-1})	Assignments	Electronic spectra (cm^{-1})	Assignments
Na[VOF$_2$(CysH)(H$_2$O)]	980 (s)	ν(V=O)		
	523 (s)	ν(V–F)		
	1625 (s, br)	ν_{as}(COO$^-$) + δ(H–O–H)		
	1387 (s)	ν_s(COO$^-$)		
	475 (m)	ν(V–O)		
	372 (s)	ν(V–S)		
	1507 (m)	δ_s(NH$_3$$^+$)		
	744 (m)	ρ_r(H$_2$O)		
	3420 (m)	ν(O–H)		
NH$_4$[VOF$_2$(CysH)(H$_2$O)]	976 (s)	ν(V=O)	12400	$3d^*_{xy} \rightarrow 3d^*_{xz}$, $3d^*_{yz}$
	521 (s)	ν(V–F)	16000	$3d^*_{xy} \rightarrow 3d^*_{x^2-y^2}$
	1625 (s, br)	ν_{as}(COO$^-$) + δ(H–O–H)	40800	$3d^*_{xy} \rightarrow 3d^*_{z^2}$
	1384 (s)	ν_s(COO$^-$)		
	470 (m)	ν(V–O)		
	371 (s)	ν(V–S)		
	1484 (m)	δ_s(NH$_3$$^+$)		
	741 (m)	ρ_r(H$_2$O)		
	3420 (m)	ν(O–H)		
	1427 (s)	ν(N–H)ν_4		
NH$_4$[VOF$_3$(AlanH)(H$_2$O)]	967 (s)	ν(V=O)	12410	$3d^*_{xy} \rightarrow 3d^*_{xz}$, $3d^*_{yz}$
	520 (s)	ν(V–F)	16010	$3d^*_{xy} \rightarrow 3d^*_{x^2-y^2}$
	1605 (s)	ν_{as}(COO$^-$)	40850	$3d^*_{xy} \rightarrow 3d^*_{z^2}$
	1381 (s)	ν_s(COO$^-$)		
	483 (m)	ν(V–O)		
	1118 (m)	ρ_r(NH$_3$$^+$)		
	740 (m)	ρ_r(H$_2$O)		
	3418 (m)	ν(O–H)		
	1434 (s)	ν(N–H)ν_4		
Na[VOF$_3$(SerH$_2$)(H$_2$O)]	970 (s)	ν(V=O)		
	525 (s)	ν(V–F)		
	1625 (s, br)	ν_{as}(COO$^-$) + δ(H–O–H)		
	1398 (s)	ν_s(COO$^-$)		
	472 (m)	ν(V–O)		
	1487 (m)	δ_s(NH$_3$$^+$)		
	1115 (m)	ρ_r(NH$_3$$^+$)		
	746 (m)	ρ_r(H$_2$O)		
	3415 (m)	ν(OH)		
	3450 (m)	ν(O–H) (from serine)		
NH$_4$[VOF$_3$(SerH$_2$)(H$_2$O)]	965 (s)	ν(V=O)	12405	$3d^*_{xy} \rightarrow 3d^*_{xz}$, $3d^*_{yz}$
	530 (s)	ν(V–F)	16030	$3d^*_{xy} \rightarrow 3d^*_{x^2-y^2}$
	1625 (s, br)	ν_{as}(COO$^-$) + δ(H–O–H)	40845	$3d^*_{xy} \rightarrow 3d^*_{z^2}$
	1387 (s)	ν_s(COO$^-$)		
	483 (m)	ν(V–O)		
	1485 (m)	δ_s(NH$_3$$^+$)		
	1120 (m)	ρ_r(NH$_3$$^+$)		
	740 (m)	ρ_r(H$_2$O)		
	3418 (m)	ν(O–H)		
	3450 (s)	ν(O–H) (from serine)		
	1435 (s)	ν(N–H)ν_4		
K[VOF$_3$(SerH$_2$)(H$_2$O)]	973 (s)	ν(V=O)		
	522 (s)	ν(V–F)		
	1625 (s, br)	ν_{as}(COO$^-$) + δ(H–O–H)		
	1390 (s)	ν_s(COO$^-$)		
	478 (m)	ν(V–O)		
	1485 (m)	δ_s(NH$_3$$^+$)		
	1118 (m)	ρ_r(NH$_3$$^+$)		
	743 (m)	ρ_r(H$_2$O)		
	3420 (m)	ν(O–H)		
	3450 (s)	ν(O–H) (from serine)		

Table 2
Analytical data and room-temperature magnetic moments of complexes

Compound	Yield (%)	Na or K	Analysis [a] (%)					μ_{eff} (B.M.)
			V	F	C	H	N	
Na[VOF$_2$(CysH)(H$_2$O)]	72	8.53 (8.64)	19.29 (19.14)	14.15 (14.28)	13.60 (13.54)	2.99 (3.04)	5.19 (5.26)	1.57
NH$_4$[VOF$_2$(CysH)(H$_2$O)]	68	–	19.61 (19.50)	14.46 (14.55)	13.81 (13.79)	4.69 (4.64)	10.85 (10.73)	1.57
NH$_4$[VOF$_3$(AlanH)(H$_2$O)]	64	–	20.40 (20.45)	22.79 (22.88)	14.40 (14.46)	5.30 (5.27)	11.19 (11.25)	1.47
Na[VOF$_3$(SerH$_2$)(H$_2$O)]	61	8.45 (8.51)	18.84 (18.86)	21.09 (21.11)	13.25 (13.34)	3.33 (3.36)	5.23 (5.19)	1.51
NH$_4$[VOF$_3$(SerH$_2$)(H$_2$O)]	65	–	19.24 (19.21)	21.55 (21.50)	13.54 (13.59)	4.86 (4.95)	10.51 (10.57)	1.49
K[VOF$_3$(SerH$_2$)(H$_2$O)]	65	13.67 (13.66)	17.89 (17.80)	19.85 (19.92)	12.53 (12.59)	3.29 (3.18)	4.91 (4.89)	1.51

[a] Calculated values are given in parentheses.

six-membered ring being coordinated through –S and –O atoms.

A representative compound, NH$_4$[VOF$_2$(CysH)(H$_2$O)], when dissolved in water exhibited three bands in its electronic absorption spectrum at 12 400 (ϵ = 16 1 mol^{-1} cm^{-1}), 16 000 (ϵ = 9 1 mol^{-1} cm^{-1}) and 40 800 cm^{-1} (ϵ = 421 1 mol^{-1} cm^{-1}) (Table 1). The first two bands have been assigned to $(3d^*_{xy}) \rightarrow (3d^*_{xz}, 3d^*_{yz})$ and $(3d^*_{xy}) \rightarrow (3d^*_{x^2-y^2})$ transitions, respectively, while the third band above 40 000 cm^{-1} has been assigned to a $(3d^*_{xy}) \rightarrow (3d^*_{z^2})$ transition. This is typical of six-coordinated oxovanadium(IV) species [21]. The peak positions match well with those reported for oxovanadium(IV) complexes [21].

Besides cysteine, L-alanine and L-serine were the other amino acids involved in the present study. The colour of the alanine and serine complexes of VO^{2+} is virtually similar to that of the cysteine complexes. Chemical analyses confirmed the occurrence of the metal and fluoride in a 1:3 atomic ratio in these compounds.

The vibrational spectra of the compounds containing alanine and serine ligands showed absorptions due to V=O, V–F and coordinated water, with their positions and intensities being similar to those of the corresponding cysteine complexes (Table 1). However, both alanine and serine were found to occur in a zwitterionic form in the respective cases. This, and the absence of any coordination through nitrogen, was clearly indicated by the appearance of a ρ_r(NH$_3^+$) mode [22] at 1118 (m) cm^{-1} for NH$_4$[VOF$_3$(AlanH)(H$_2$O)] and ca. 1120 cm^{-1} for A[VOF$_3$(SerH$_2$)(H$_2$O)] (A = Na, NH$_4$ or K). In addition, the occurrence of ν_{as}(COO$^-$), ν_s(COO$^-$) and ν(V–O) at ca. 1615 (s), ca. 1390 (s) and ca. 475 (m) cm^{-1}, respectively, provided support to the contention that in each case the amino acid ligand is coordinated to the metal centre through the O atom of the carboxylate group with the ligand unidentate [20,22]. The band at

ca. 1435 cm^{-1} observed for the ammonium salts was assigned to the [ν(N–H)ν_4] mode of the NH$_4^+$ ion.

It is relevant to mention that the coordination of a side-chain hydroxy group of the amino acid with a metal is unlikely because structures gave no evidence for such coordination [2b,23], although the results of several thermodynamic studies were interpreted in terms of a weak metal–hydroxy bond [24]. In the present investigation a comparison of the ν(O–H) mode of the free ligand [25] and coordinated serine revealed no significant change in the band position, indicating that the OH group did not coordinate to the metal.

The complexes are all paramagnetic with the effective room-temperature magnetic moments lying in the range 1.47–1.57 μ_B (Table 2). Although clearly indicative of the presence of vanadium(IV), the values are somewhat lower than normal. The ESR spectra of freshly prepared aqueous solutions of NH$_4$[VOF$_2$(CysH)(H$_2$O)], NH$_4$[VOF$_3$-(AlanH)(H$_2$O)] and NH$_4$[VOF$_3$(SerH$_2$)(H$_2$O)] recorded at ambient temperature exhibited an eight-line pattern, each characteristic of a mononuclear vanadium(IV) (I = 7/2) complex with g_{av} being 1.986, 1.982 and 1.981, respectively. The ESR results suggest the occurrence of an oxovanadium(IV) species in an octahedral ligand environment [21].

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