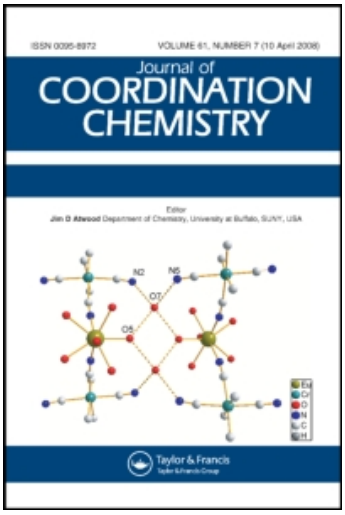

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Synthesis and spectroscopic characterization of hydroxylamido/amino acid complexes of oxovanadium(V)§

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A series of mixed ligand oxovanadium(V) complexes of the type $[VO(NH_2O)_2(aa)]$, containing the hydroxylamido ligand and simple amino acids, were prepared and characterized. Seven of these complexes, with aa = valine, leucine, isoleucine, phenylalanine, tryptophan, cysteine and methionine, were described for the first time. Their infrared and Raman spectra, together with those of the previously investigated similar species with aa = glycine, serine, threonine and alanine, and those of the related $[VO(NH_2O)_2(imidazole)_2]Cl$ complex, were recorded and assigned. The spectroscopic behavior of the new complexes is similar to that of the other five, whose structures has been determined by X-ray crystallography, suggesting an identical structure for the full series of complexes. The spectroscopic results also give a better characterization of the vibrational behavior of the interesting O–N– "side-on" bonded hydroxylamido ligand.

Keywords: Oxovanadium(V); Hydroxylamido complexes; Synthesis; IR spectra; Raman spectra; Vibrational behavior

1. Introduction

Vanadium is a trace element and, although its essentiality for higher forms of life remains controversial [1–4], it can play an important role in metalloenzymes and in insulin regulation [1, 4–8].

Peroxovanadium complexes received increasing attention during the last years as they are involved as intermediates in halide oxidation by vanadate-dependent peroxidases [1, 4, 9–12] and, additionally, some of them present interesting pharmacological properties [13, 14]. Hydroxylamine, H_2NOH, which is isoelectronic with hydrogen peroxide, H_2O_2, is capable of coordinating to vanadium, and different complexes containing the hydroxylamido ligand, NH_2O^-, have been characterized [15, 16]. Interestingly, the ligand present in amavadin, the non-oxo vanadium(IV) complex

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§Dedicated to Prof. Alfredo Mederos on the occasion of his retirement as Professor of Inorganic Chemistry, Universidad de La Laguna, Tenerife, Spain.

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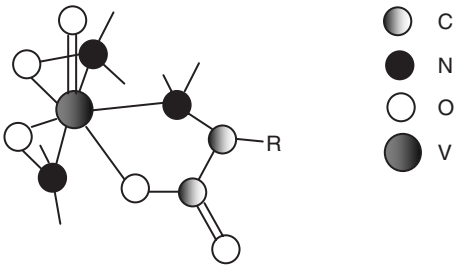

Figure 1. Schematic representation of the structure of the investigated $[VO(H_2NO)_2(aa)]$ complexes.

isolated from the mushroom *Amanita muscaria*, is the bis(propionate) derivative of hydroxylamide [11, 16].

Peroxovanadium complexes have been better characterized than hydroxylamido complexes, but the available information suggests strong similarities with regard to structural peculiarities, coordination numbers and reactivity [17, 18].

To advance understanding of the general characteristics of oxovanadium(V) hydroxylamido complexes, we have now prepared a number of mixed-ligand complexes containing this ligand and different amino acids and investigated their vibrational spectroscopic behavior. Only four complexes of this type, of stoichiometry $[VO(NH_2O)_2(aa)] \cdot nH_2O$, with aa = glycine (gly) and serine (ser) [19] or aa = alanine (ala) and threonine (thr) [20], have previously been characterized. We have now added complexes containing valine (val), leucine (leu), isoleucine (ile), phenylalanine (phe), tryptophan (trp), cysteine (cys) and methionine (met) to this list. Additionally, for comparative purposes we have also characterized a similar complex, $[VO(NH_2O)_2(imid)_2]Cl$, containing two imidazoles (imid) for which a crystal structure has been previously determined [19].

The complete structural characterization of the five previously prepared complexes showed that the vanadium is seven-coordinate structure adopting a distorted trigonal-bipyramidal environment, as depicted in figure 1. A similar structure has been found in other closely related complexes such as $[VO(NH_2O)(H_2O)(dipic)]$ [21] or $[VO(Me_2NO)(H_2O)(dipic)]$ [18] (dipic = dipicolinic acid, pyridin-2,6-dicarboxylic acid). In all cases the hydroxylamido anion, NH_2O^-, is O,N-coordinated in the "side-on" fashion.

2. Experimental

2.1. *Materials*

NH_4VO_3, NaOH and $NH_2OH \cdot HCl$ were purchased from Carlo Erba, the amino acids from Sigma and imidazole from Riedel de Häen, and were used as supplied.

2.2. *Synthesis and characterization of the complexes*

A general procedure derived from previously described synthetic routes [19, 20] was used. About 4 or 5 mM of NH_4VO_3, together with variable amounts of NaOH

Table 1. Stoichiometry and analytical data for the prepared complexes (values in parentheses correspond to the theoretically calculated values).

Complex	MW	%C	%H	%N
$[VO(NH_2O)_2(gly)] \cdot H_2O$	223.07	11.06 (10.77)	4.20 (4.52)	19.10 (18.84)
$[VO(NH_2O)_2(ala)] \cdot 2H_2O$	255.11	15.00 (14.12)	5.40 (5.53)	16.75 (16.47)
$[VO(NH_2O)_2(val)]$	247.13	23.80 (24.30)	5.02 (4.89)	16.88 (17.00)
$[VO(NH_2O)_2(leu)] \cdot H_2O$	279.15	26.55 (25.82)	6.92 (6.50)	15.15 (15.05)
$[VO(NH_2O)_2(ile)]$	261.12	28.25 (27.57)	5.47 (6.13)	16.78 (16.09)
$[VO(NH_2O)_2(phe)]$	295.17	36.25 (36.62)	5.05 (4.78)	14.10 (14.24)
$[VO(NH_2O)_2(trp)]$	334.17	36.59 (35.91)	3.75 (4.19)	12.99 (12.57)
$[VO(NH_2O)_2(ser)]$	235.07	15.37 (15.33)	4.54 (4.29)	17.74 (17.87)
$[VO(NH_2O)_2(thr)]$	249.10	19.15 (19.29)	4.95 (4.86)	16.58 (16.87)
$[VO(NH_2O)_2(cys)]$*	251.13	14.58 (14.35)	4.19 (4.01)	16.15 (16.73)
$[VO(NH_2O)_2(met)]$**	279.19	21.22 (21.51)	5.10 (5.05)	14.87 (15.05)
$[VO(NH_2O)_2(imid)_2]Cl$	302.55	23.75 (23.82)	4.18 (3.99)	27.34 (27.77)

*S (found) = 12.83 (calculated = 12.77%).
**S (found) = 11.60 (calculated = 11.48%).

(amounts estimated from the titration curve and p*K*-values of the respective amino acids [22] and must be sufficient to ensure neutrality after the final addition of $NH_2OH \cdot HCl$) were dissolved in the minimum necessary volume of distilled water (*ca.* 20 mL). To this solution the corresponding amino acid, in the approximate proportion amino acid/$NH_4VO_3 \approx 3.0$, was added in small portions. The obtained solution was cooled to 4°C and solid $NH_2OH \cdot HCl$ (in the approximate proportion $NH_2OH \cdot HCl/NH_4VO_3 \approx 5.2$) was added under constant stirring until dissolution is complete. The resulting clear solution was held at 4°C and crystallization usually occurs after a few hours. The precipitate was separated by filtration, washed with small portions of cold water and absolute ethanol, and finally dried under vacuum. Only for complexes containing tryptophan and isoleucine was it difficult to obtain totally pure complexes, as they were always contaminated with small amounts of the respective amino acids, even when reducing the proportion of them employed in the syntheses.

The $[VO(NH_2O)_2(imid)_2]Cl$ was prepared in a similar way [19], but employing $NaVO_3$ instead of NH_4VO_3.

The synthetic procedure allows rapid and easy preparation of these mixed ligand complexes in a reasonable yield (usually between 50% and 65%). The pH of the reaction media seems to be critical to ensure purity and adequate yields. It is, therefore, very important to have a practically neutral solution after the addition of $NH_2OH \cdot HCl$ to the vanadate/amino acid mixture (cf. also [19]).

All the obtained complexes were characterized by elemental analysis using a Carlo Erba model EA 1108 elemental analyzer. The obtained results are presented in table 1. In all the complexes the oxovanadium(V) cation is coordinated to two hydroxylamido ligands and to one deprotonated amino acid. Three of the prepared complexes contain water of crystallization; the others are anhydrous.

2.3. *Spectroscopic measurements*

FTIR spectra in the spectral range between 4000 and 400 cm^{-1} were measured as KBr pellets on a Bomem M 102 instrument. Raman spectra were recorded with the FRA 106 accessory of a Bruker IF 66 FTIR spectrophotometer. The 1064 nm line of a Nd: YAG

solid state laser was used for excitation. Not all of the prepared complexes gave good Raman spectra, as some of them have a poor signal to noise ratio, probably from partial decomposition of the samples during measurement.

3. Results and discussion

3.1. *Vibrational spectra*

There is little information about the vibrational-spectroscopic behavior of hydroxylamido complexes [23, 24]. Detailed spectroscopic information on the hydroxylamine molecule in the gas phase is available (cf. for example [25, 26] and references therein) and on the basis of these data it seems possible to attempt the vibrational analysis of the O,N-bonded hydroxylamido ligands in the investigated complexes.

Assuming C_s symmetry for the free molecule [25, 26] the irreducible representation for the vibrational modes of H_2N–OH can be written as $\Gamma_{Cs} = 6A' + 3A''$, and all these species show both infrared and Raman activity [24]. The observed experimental vibrational frequencies (in cm^{-1}) are as follows: ν(OH), $\nu_1(A') = 3650$; $\nu_s(NH_2)$, $\nu_2(A') = 3294$; $\delta(NH_2)$, $\nu_3(A') = 1604$; δ(NOH), $\nu_4(A') = 1353$; $\rho_w(NH_2)$, $\nu_5(A') = 1115$; ν(NO), $\nu_6(A') = 895$; $\nu_{as}(NH_2)$, $\nu_7(A'') = 3358$; $\rho_\tau(NH_2)$, $\nu_8(A'') = 1294$ and τ (OH), $\nu_9(A'') = 386$. After formation of the hydroxylamido ligand and coordination to the metal center three of these vibrations (ν_1, ν_4 and ν_9) are no longer present, and only vibrational modes related to the NH_2-moieties and the N–O stretching motion remain to be identified.

FTIR spectra of all the prepared compounds are relatively complex, especially due to the number of bands of the bonded amino acids. On the contrary, the corresponding Raman spectra are relatively simple, presenting a reduced number of strong and medium intensity lines in the spectral range between 1200 and 100 cm^{-1}. As an illustration, the FTIR spectrum of $[VO(NH_2O)_2(val)]$ is shown in figure 2, whereas the Raman spectrum of the same complex, in the range of interest, is presented in figure 3.

As it seems very difficult to attempt a complete assignment of all measured IR and Raman bands, we have only tried to identify those related to the H_2NO^- ligand, to the

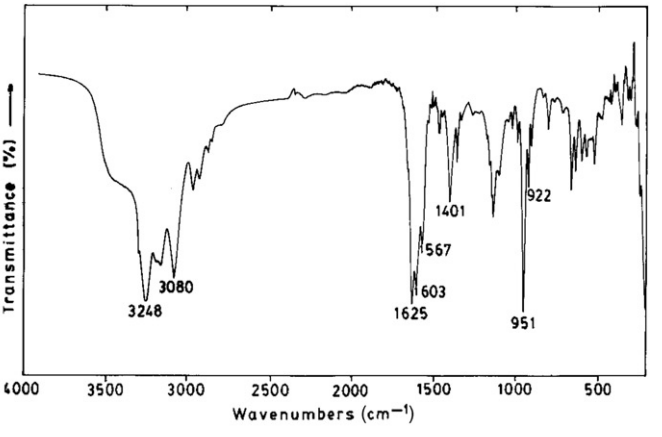

Figure 2. FTIR spectrum of $[VO(H_2NO)_2(val)]$ (wavenumbers of some of the most characteristic bands are identified).

VO^{3+} moiety and to some of the most important and characteristic vibrations of each of the bonded amino acids (and of imidazole in the case of the $[VO(NH_2O)_2(imid)_2]Cl$ complex). For this purpose, we have also measured the FTIR spectra of the free amino acids and used information provided by standard references [24, 27, 28], as well as by previous studies on simple amino acid complexes, performed in our laboratories [29–33]. Additionally, IR spectral data on simple hydroxylammonium salts, such as $[NH_3OH]Cl$ and $[NH_3OH]_2SO_4$, are also available for comparison [34].

The analysis and the proposed assignment of the FTIR spectra of the 11 complexes containing amino acids are shown in tables 2–4. On the basis of the obtained results, a general discussion on the vibrational behavior is possible, as follows:

- The higher frequency range is dominated, in all cases, by the stretching vibrations of the NH_2-moieties. By comparison with the position found for these vibrations in

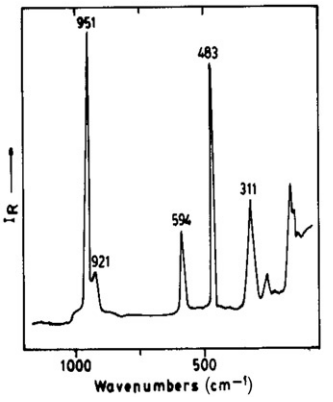

Figure 3. FT-Raman spectrum of $[VO(H_2NO)_2(val)]$ in the spectral range between 1200 and 100 cm^{-1} (wavenumbers of some of the most characteristic bands are identified).

Table 2. Assignment of the most characteristic IR bands of the $[VO(NH_2O)_2(aa)]$ complexes with aa = glycine, alanine, valine, leucine and isoleucine (band positions in cm^{-1}).

gly	ala	val	leu	ile	Assignment
3296 vs	3246 vs	3248 vs	3263 s	3276 vs	$\nu(NH_2)$ aa
3114 s	3087 s	3158 m	3187 s	3185 m	$\nu_{as}(NH_2)$ hd
2980 s	3051 s	3080 s	3057 s	3082 s	$\nu_s(NH_2)$ hd
	2968 s	2964 m	2955 m	2967 m	$\nu_{as}(CH_3)$
1639 vs	1626 vs	1625 vs	1604 vs	1630 vs	ν(C=O)
1585 vs	1604 vs	1603 s	1583 s	1610 m	$\delta(NH_2)$ aa
1557 s	1552 sh	1567 w	1560 sh	1561 m	$\delta(NH_2)$ hd
	1463 m	1465 w	1470 m	1459 m	$\delta_{as}(CH_3)$
1396 vs	1402 s	1401 m	1407 s	1401 s	ν(C–O)
1360 m	1354 m	1356 w	1347 m	1353 m	$(CH_2) + \nu(C–CO_2)$
1137s	1132 sh	1134 m	1135 m	1121 m	ν(C–C)
1103 vs	1113 vs	1100 m	1091 m	1094 m	ν(CN)
972 vs	959 vs	951 vs	940 vs	952 vs	$\nu(VO^{3+})$
922 s	937 s	922 m	925 vs	940 vs	ν(N–O)
640 s	647 s	658 m	662 m	647 m	$\rho(CO_2) + \rho(NH_2)$
595 s	581 m	595 m	584 m	588 m	ν(V–O)

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; aa: amino acid; hd: hydroxylamido.

Table 3. Assignment of the most characteristic IR bands of the $[VO(NH_2O)_2(aa)]$ complexes with aa = phenylalanine, serine, threonine and tryptophan (band positions in cm^{-1}).

phe	Ser	thr	trp	Assignment
			3407 vs	ν(NH)trp
	3390 s	3423 s		ν(OH)
3243 m	3245 vs	3244 vs	3204 m	$\nu(NH_2)$ aa
3187 s	3166 w	3156 m	3122 w	$\nu_{as}(NH_2)$ hd
3066 m	3068 s	3059 m		$\nu_s(NH_2)$ hd
2928 m			2940 w	$\nu_{as}(CH_2)$
1610 vs	1650 vs	1633 vs	1626 vs	ν(C=O)
1582 s	1607 m	1595 m	1592 m	$\delta(NH_2)$ aa
1560 sh	1551 w	1550 sh	1540 sh	$\delta(NH_2)$ hd
1454 w	1448 w		1457 m	$\delta_{sciss}(CH_2)$
1408 s	1402 m	1405 s	1401 s	ν(C–O)
1345 w	1366/1342 w	1355 w	1344 m	$(CH_2) + \nu(C–CO_2)$
1146 m	1141 m	1130 s	1137 s	ν(C–C)
1097 m	1093 m	1090 m	1094 m	ν(CN)
956 m	963 vs	963 vs	952 vs	$\nu(VO^{3+})$
926 s	928 m	933 m	926 m	ν(N–O)
660 w	652 s	641 m	641 m	$\rho(CO_2) + \rho(NH_2)$
585 w	593 m	595 w	578 w	ν(V–O)

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; aa: amino acid; hd: hydroxylamido.

Table 4. Assignment of the most characteristic IR bands of the $[VO(NH_2O)_2(aa)]$ complexes with aa = cysteine and methionine (band positions in cm^{-1}).

cys	met	Assignment
3243 s	3235 vs	$\nu(NH_2)$ aa
3175 w	3195 w	$\nu_{as}(NH_2)$ hd
3050 s	3045 s	$\nu_s(NH_2)$ hd
	2960 w	$\nu_{as}(CH_3)$
1626 vs	1625 vs	ν(C=O)
1561 s	1603 s	$\delta(NH_2)$ aa
	1578 sh	$\delta(NH_2)$ hd
1390 vs	1418 s	ν(C–O)
1353 w	1356 m	$(CH_2) + \nu(C–CO_2)$
	1176 w	ν(C–C)
1096 s	1116 m	ν(CN)
961 vs	957 vs	$\nu(VO^{3+})$
930 s	942 vs	ν(N–O)
	770 w	ν(C–S–C)
701 w		ν(C–S)
643 s	661 w	$\rho(CO_2) + \rho(NH_2)$
585 m	585 w	ν(V–O)

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; aa: amino acid; hd: hydroxylamido.

Cu(II) amino acid complexes [29–33], we suggest that the NH_2 vibrations of the amino groups of the amino acids are located at higher energies than those of the hydroxylamido groups. For these groups we could usually assign the symmetric and antisymmetric vibration. However, eventually a partial mixing between the vibrations of both NH_2 moieties, especially in the spectral range around 3200 cm^{-1}, cannot be

totally excluded. In the case of tryptophan this high frequency region is more complicated by the additional presence of the strong ν(NH) band of the pyrrole ring.

- In the case of the complexes of glycine, alanine and leucine, which contain hydration water, this high frequency region shows some additional features and band broadening, obviously related to the ν(O–H) stretches. Interestingly, the corresponding $\delta(H_2O)$ mode, expected to lie around 1650–1600 cm^{-1}, does not introduce important modifications in this spectral range, probably due to its weak intensity in comparison with the other bands found in this region.
- The other spectral range of special interest is around 1600 cm^{-1}. In this region one may expect the carbonyl stretching vibration of the amino acids and the scissoring deformational modes of the NH_2 groups. In this region three features are usually observed, as can be seen in figure 2 for the case of $[VO(NH_2O)_2(val)]$, i.e. one very strong, one strong and one weak band or a shoulder. On the other hand, a band assignable to the ν_s(C–O) stretching vibration, involving the metal-bonded oxygen atom, could be clearly identified in all cases.
- To identify the correct position of the ν(C=O) vibration located in the band triplet, we compared carboxylate vibrations found in the free amino acids with those in the respective complexes. This comparison is presented in table 5. The "free" amino acids exist as zwitterions in the crystalline state; thus, one expects two vibrations for the carboxylate moiety present in these systems, $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$. After coordination, one should expect a lowering of the frequency of one of these bands due to the generation of the V–O bond and increase of the other, because a C–O double bond is partially reconstructed. As shown from the data presented in table 5, the band assigned to $\nu_s(COO^-)$ in the "free" acid suffers a small shift to lower frequencies in all cases, except for the methionine complex, in agreement with the participation of one C–O bond in metal binding. Contrarily, and as expected, the other band shifts to higher frequency after complex formation. In conclusion, this analysis clearly supports the assignment, which relates the highest energy component of the above-mentioned triplet to the ν(C=O) stretching vibration.
- For the two NH_2 deformational modes, we have applied the same criterion as in the stretching region, i.e. we assumed that the deformational mode of the hydroxylamido NH_2 moiety lies at lower energy than that of the amino group of the amino acid, and the intensity of the hydroxylamido band is appreciably lower than that of the amino acid.
- Some other characteristic amino acid bands such as CH_3- and CH_2-modes, ν(C–C) and ν(CN) vibrations could also be identified. In the case of the sulfur-containing amino acids, also the characteristic ν(C–S) (cys) and ν(C–S–C) (met) stretching modes could be assigned. In the case of cysteine the ν(S–H) vibration was not found, in agreement with its usual very low intensity in the IR spectrum [27, 35]. In the two complexes with hydroxyl residues (serine, threonine) the ν(OH) stretching vibrations could be clearly identified, in agreement with the fact that this group is not involved in coordination.
- The hydroxylamido N–O stretching band is expected to lie between 920 and 1050 cm^{-1} in metallic complexes, irrespective of the coordination mode of the NH_2–NO^- ligand [23]. In the case of crystalline hydroxylammonium salts it lies at 998 cm^{-1} in $[NH_3OH]Cl$ and at 1000 cm^{-1} in $[NH_3OH]_2(SO_4)$ [34]. In our complexes, the band related to this vibration is always found very close to the strong $\nu(VO^{3+})$ stretch as a strong or medium intensity band between 922 and 942 cm^{-1}.

Table 5. Comparison of the carboxylate stretching vibrations (in cm^{-1}) in the "free" amino acids and in the investigated complexes.

Amino acid/Complex	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$
glycine	1608	1412
$[VO(NH_2O)_2(gly)]\cdot H_2O$	1639	1396
alanine	1605	1413
$[VO(NH_2O)_2(ala)]\cdot 2H_2O$	1626	1402
valine	1586	1426
$[VO(NH_2O)_2(val)]$	1625	1401
leucine	1583	1410
$[VO(NH_2O)_2(leu)]\cdot H_2O$	1604	1407
isoleucine	1602	1417
$[VO(NH_2O)_2(ile)]$	1630	1401
phenylalanine	1562	1411
$[VO(NH_2O)_2(phe)]$	1610	1408
serine	1597	1412
$[VO(NH_2O)_2(ser)]$	1650	1402
threonine	1626	1417
$[VO(NH_2O)_2(thr)]$	1633	1405
tryptophan	1590	1412
$[VO(NH_2O)_2(trp)]$	1626	1401
cysteine	1623	1399
$[VO(NH_2O)_2(cys)]$	1626	1390
methionine	1583	1409
$[VO(NH_2O)_2(met)]$	1625	1418

- The V–O stretching vibration of VO^{3+} constitutes one of the strongest IR bands and is, therefore, easy to identify. In the investigated complexes it is between 940 and 972 cm^{-1}, indicating the presence of a relatively strong metal–oxygen bond. The position of this band is comparable to that found in a number of oxodiperoxovanadate complexes [36, 37] as well as in oxovanadium(V) complexes of "oxine" derivatives [38]. In the cases for which structural data are available [19, 20], the V–O bond lengths in the complexes are comparable and, consequently, the observed differences must be ascribed to packing effects in the solid state (cf. also [20]).
- Finally, all the investigated complexes present a characteristic band in the spectral range between 578 and 595 cm^{-1}, assigned to a V–O stretch involving the hydroxylamido ligand. In the case of vanadium(V) peroxo complexes the V–O bands involving the peroxo ligand are in comparable ranges [37–40] and similar ranges are also found in the case of chromium(VI) peroxo complexes [41].

In order to support additionally some of the assignments it was interesting to investigate the vibrational behavior of $[VO(NH_2O)_2(imid)_2]Cl$. In this case the absence of amino acid ligand could simplify some of the most interesting spectral ranges. The corresponding data are shown in table 6.

Most of the characteristic imidazole vibrations were assigned on the basis of known spectral data [42]. The hydroxylamido NH_2-stretches are seen as a unique band at 3220 cm^{-1}, somewhat higher than its position in amino acid complexes. Interestingly, the corresponding $\delta(NH_2)$ vibration is found as a relatively weak band, superimposed with a stronger imidazole ring mode, but also confirming the behavior of this mode in the complexes of the amino acid series.

Table 6. Assignment of the most characteristic IR bands of the $[VO(NH_2O)_2(imid)_2]Cl$ complex (band positions in cm^{-1}).

Band position	Assignment
3220 vs	$\nu(NH_2)$ hd
3143 s	ν(CH) imid
3031 vs	ν(NH) imid
1590 w	δ(NH) imid
1534 w	$\delta(NH_2)$ hd
1502 m	νring imid
1431 m	δ(NH) imid
1327 m	δ(CH) imid
1259 m, 1231 w	νring imid
1138 s	δ(NH) imid
1097 s, 1069 vs	δ(CH) imid
973 sh	νring imid
953 vs	$\nu(VO^{3+})$
919 w	ν(N–O) hd
750 m	γ(CH) imid
661 sh, 650 m	τ(NH) imid
614 m	γ(NH) imid
585 w	ν(V–O)

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; imid: imidazole; hd: hydroxylamido.

The $\nu(VO^{3+})$ stretch lies in the same range as in the other complexes and also appears in this case as one of the strongest IR bands. Also, the ν(V–O) band is found in the expected range, whereas the ν(N–O) band is somewhat weaker than in the amino acid complexes.

The behavior of a ring mode located at 936 cm^{-1} in free imidazole, which is very sensitive to complexation [43], is very interesting too. As usual [43–45], after complex formation this band is displaced to higher energy and shows an important intensity lowering. In the present case it is only seen as a weak shoulder at 973 cm^{-1}, on the high energy side of the strong $\nu(VO^{3+})$ band.

Finally, we have also performed an analysis of the best seven Raman spectra which we could obtain from the investigated complexes. The data and the proposed band assignments are presented in table 7.

Practically all these spectra are dominated by two strong Raman peaks. One of them, usually the strongest, is related to the $\nu(VO^{3+})$ stretch. The second of the strongest lines is found around 480 cm^{-1}, and will be discussed later. The ν(N–O) is found in all spectra, but is a very weak signal at the lower energy side of the strong $\nu(VO^{3+})$ peak. The position of the ν(V–O) stretch is clearly confirmed by its presence in the Raman spectra, as a medium intensity line with an energy comparable to that found in the IR spectra. In the regions related to NH_2-vibrations, signals were not found, in agreement with its expected very low intensity in the Raman effect [27].

The very strong Raman feature at 480 cm^{-1}, which has no IR counterpart in any of the measured spectra, can be assigned, tentatively, to the ν(V–N) stretching vibration of the bonded hydroxylamido ligand. Regarding the other relatively strong Raman line found at about 310 cm^{-1}, its origin is uncertain but may be related to one of the V–O motions of the bonded amino acids [24].

Table 7. Assignment of the most characteristic Raman bands of the $[VO(NH_2O)_2(aa)]$ complexes with aa = valine, leucine, isoleucine, phenylalanine, threonine, cysteine and methionine, and location of other important Raman bands.

val	leu	ile	phe	thr	cys	met	Assignment
951 vs	945 vs	947 vs	957 vs	963 vs	956 vs	963 vs	$\nu(VO^{3+})$
921 w	928 w	920 w	922 w	935 w	935 w	945 sh	ν(N–O)
594 m	585 vw	594 m	591 m	595 m	582 m	578 m	ν(V–O)
483 vs	486 vs	486 vs	482 vs	487 vs	480 vs	475 vs	ν(V–N)
311 s	–	311 s	307 s	300 s	314 s	316 s	(?)
Other bands							
358 w	429 m	820 w	1603 m	803 w	2666 m	770 w	cf. text
254 w	346 m	675 w	1582 w	342 w	700 w	730 m	
162 s	334 m	285 w	1031 m	166 m	509 w	650 w	
	166 s	130 m	1001 vs		160m	253 s	
			773 w				
			620 m				
			307 s				
			243 w				
			186 s				

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.

In some of the measured complexes, the Raman spectra contain some other interesting information. In $[VO(NH_2O)_2$ (phe)] the relatively intense bands found at 1031 and 1011 cm^{-1} are surely related to δ(CH) motions in the phenyl ring, whereas other ring modes give the bands at 1603 and 1582 cm^{-1} [27, 28]. In the case of the cysteine complex the ν(S–H) vibration is seen as a medium intensity line at 2666 cm^{-1}, whereas the corresponding ν(C–S) mode is observed as a weak signal at 700 cm^{-1}. For the methionine complex the ν(CSC) stretching could also be identified in the Raman spectrum, at 770 cm^{-1}. Other signals lying at lower frequencies are not easy to assign, as they are usually strongly coupled motions including internal skeletal or deformational modes and external (''lattice'') vibrations.

4. Conclusions

Seven new oxovanadium(V) complexes of the type $[VO(NH_2O)_2(aa)]$, containing the hydroxylamido anion, NH_2O^-, coordinated in the O,N-''side-on'' mode and different amino acids (aa), coordinated through N (amino) and O(carboxylate) atoms, were prepared. Although it was not possible to obtain crystals adequate for crystallographic studies for these new complexes, the analytical data confirm a similar stoichiometry and the vibrational-spectroscopic behavior clearly demonstrate an identical structure to that reported for the analogous complexes of known structure, previously described, and schematized in figure 1.

The characteristic $\nu(VO^{3+})$ stretching vibration, observed as one of the strongest signals in both the infrared and Raman spectra was found to lie between 942 and 972 cm^{-1}. Detailed spectroscopic information for the ''side-on'' bonded NH_2O^- anion could be established here for the first time.

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