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(Article begins on next page)
Thermodynamic, spectroscopic and DFT description of oxidovanadium(IV) complexes with malate and tartrate in aqueous solution

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ABSTRACT

This investigation deals with coordination compounds of oxidovanadium(IV) with L-malic and L-tartaric acids in aqueous solution. The different binary systems are studied by potentiometric, spectroscopic techniques and DFT calculation in a wide concentration range and with different metal/ligand ratios. Electronic paramagnetic resonance spectroscopy (EPR) and molecular absorption spectrophotometry are employed. A speciation model is proposed for the metal/ligand systems elaborating the potentiometric data and the actuality of the model proposed was confirmed by the comparison of the speciation distribution with the nature and the intensity of EPR and UV-vis spectra. This approach lead us to revise the speciation models previously proposed identifying the dinuclear species $M_2L_2H_n$ as predominant, for both vanadyl-ligand systems, also in case of high ligand excess. For each system investigated the individual spectrum of the relevant species is estimated and a careful exam of electronic spectra of vanadyl complexes provided some information about the structure-spectra relation.
Keywords
Vanadium, Carboxylate ligands, UV-visible spectroscopy, EPR spectroscopy, Potentiometry, DFT calculations.

1. Introduction

Our attention is addressed to a systematic investigation of coordination compounds between vanadyl oxido cation and carboxylic acids and to their structural characterisation by means of spectroscopic techniques. In previous investigations [1,2], dealing with the vanadyl chemistry in water solution, the joint elaboration of potentiometric and spectroscopic data obtained on the vanadyl-ligand containing solutions allowed us to strengthen the speciation model proposed and to achieve a deeper knowledge of the structure of complexes in solution. With the same purpose now we present the results obtained on vanadyl-ligand systems with two α-hydroxylated oligocarboxylic acids: L-malic and L-tartaric acid. Despite vanadyl-malate and tartrate systems were widely studied, some points about speciation and spectroscopic characterization of vanadyl complexes in water solution require further investigations.

There are many articles dealing with vanadyl–tartrate systems [3-16]. Jørgensen [3], Ballhausen and Gray [4], Selbin [5,6] and Baran [7] discussed the vanadyl-tartrate spectra in order to clarify the effect of the coordination and the electronic structure of the vanadyl ion. The investigations of Dunlop et al. [8], Dunhill et al. [10] and Belford et al. [11] were focused on the spectroscopic characterization of vanadyl-tartrate species. Thermodynamic studies dealing with the chemical speciation of vanadyl-tartrate systems were proposed by Tapscott et al. [9,13], Pettit et al. [12] and Micera et al. [14,16].

The more recent studies dealing the speciation and the spectroscopic characterization of vanadyl-
The ref. 14 reports a study on vanadyl complexation with D-, L- and DL-tartrate in aqueous solution with ligand to metal molar ratios of 1:1, 1:2, 1:4, and employs potentiometric and spectroscopic (UV-vis and EPR) techniques. A more recent ref. 16 reports a study of vanadyl complexation with the same ligands, but at high ligand to metal molar ratios, and employs the combination of potentiometric, spectroscopic (UV-vis and EPR) and cyclic voltammetry techniques. They propose a speciation model where the mononuclear species are predominant in solutions with high ligand to metal molar ratios.

The vanadyl-malate system was studied with potentiometric and spectroscopic techniques by Micera et al. [17] and Helena et al. [18] and a spectroscopic investigation was carried out by Selbin et al. [5]. Micera et al. [17] proposed a speciation study based on the interpretation of titration data and of EPR and electronic spectra, but no formation constants are given. A broad investigation was proposed by Helena et al. [18]. They proposed a speciation model for the vanadyl-malate system, in a wide range of concentration conditions, and elaborated the potentiometric data with the support of UV-visible, circular dichroism and EPR spectra. Nevertheless, the speciation model hypothesised provides the formation of only mononuclear species, interpretation that is not in full agreement with our experimental data.

For both the two metal-ligand systems the previous interpretations of the data relative to solutions with high ligand excess are not completely satisfying. The intensity of EPR spectra shows the presence of dinuclear species and only of a minor fraction of mononuclear ones. In order to resolve this uncertainty, in this work, the chemical models obtained from the elaboration of the potentiometric data, are sustained and optimized by the careful comparison of the speciation distribution diagrams, calculated on the basis of the model, with the spectroscopic data. The model is considered satisfying when both the nature and the intensity of each EPR and UV-vis spectra, recorded at different pH values, is in accordance with the type and the abundance of the species.
hypothesised on the basis of the model at the same pH. This approach, for the first once applied also
to EPR data, led us to propose an improved and a more comprehensive interpretation of
experimental evidence for the two metal-ligand systems. Moreover, the UV-vis spectra are
elaborated applying the speciation model in order to obtain the spectroscopic parameters of single
complex species providing interesting information on the structure of vanadyl complexes.
Additionally, we intend to check which kind of vanadyl complexes can match the speciation
proposed on the basis of potentiometric titration, by examining equilibrium structures that are
minimum in energy and that are able to reproduce an experimental observable with DFT
calculations.

2. Experimental

2.1 Chemicals

Vanadyl sulfate (vanadium(IV) oxide sulphate pentahydrate, purity ~ 96%, Riedel-de Haën or
Aldrich), stock solution (~ 0.1 mol L\(^{-1}\)) is weekly prepared without previous purification of the salt;
it is standardized by redox titration with permanganate solution [19] (Carlo Erba), followed by
photometric detection [1].

L-(−)-malic ((S)-(−)-hydroxybutanedioic acid) (purity of 99.5%) and L-(+)-tartaric (2,3-
dihydroxybutanedioic acid) (purity of 99.5%) acids are Merck products. The ligand molecule are
used without further purification and their purity are checked alkalimetrically.

Potassium and sodium chloride solutions are prepared by weighing pure salt (Fluka, p.a.). Standard
KOH and HCl solutions are prepared by diluting Merck or Fluka concentrate products and standardized against potassium hydrogenphthalate (Fluka, puriss.) and sodium carbonate (Fluka, puriss.), respectively. All solutions are prepared using grade A glassware and ultrapure water (conductivity < 0.1 µS).

2.2 Electromotive force measurements

Potentiometric measurements are performed using a Metrohm mod. 713 potentiometer (resolution of ±0.1 mV) coupled with a Metrohm 665 Dosimat burette (minimum volume deliverable of ±0.001 cm$^3$) and equipped with a Metrohm combined glass electrode (mod. 6.0222.100). For all the potentiometric measurements the electrode couple is standardized, in terms of pH = -log[H$^+$], by titrating HCl 10 mmol L$^{-1}$ solution (at the same ionic strength value as the solution under study) with standard KOH in order to determine the standard potential $E^0$ before each experiment. The electrode response in the alkaline region was verified by calculating the $pK_w$ value elaborating the titration data of the alkaline region. The potentiometric titrations are carried out in a stream of purified nitrogen gently bubbled in the titration cell to avoid O$_2$ and CO$_2$ contamination. The measurement cells are thermostated at (25±0.1°C) by means of a water circulation from a thermocryostat (mod. D1-G Haake).

The most of the potentiometric titrations are carried out in KCl aqueous solutions with ionic strength 0.1 mol L$^{-1}$. The solutions with L-tartaric acid concentration higher that 10 mmol L$^{-1}$ are prepared utilizing NaCl 0.1 mol L$^{-1}$ as background salt in order to avoid the precipitation of L-tartaric acid monopotassium salt. For the investigation of VO$^{2+}$-carboxylate systems, 25 mL of solution containing VO$^{2+}$, the carboxylate ligand and KCl (or NaCl) is titrated with KOH standard.
Each titration is at least twice repeated. The metal concentration ranges from 5 to 20 mmol L\(^{-1}\) for malate systems, from 3 to 10 mmol L\(^{-1}\) for tartrate systems. The ligand concentration ranges from 2.5 to 50 mmol L\(^{-1}\) for malate and from 3 to 60 mmol L\(^{-1}\) for tartrate system. The metal to ligand ratios are 1:1, 1:2, 1:10, 3:1 for malate system, 1:1, 1:2, 1:3, 1:4, 1:7.5 and 3:1 for tartrate system. The considered ranges of pH are 2.1 - 7.5 and 2.1 - 9.0 for malate and tartrate, respectively.

2.3 Spectrophotometric measurements

The visible molecular absorption (350-900 nm) spectra are recorded on VO\(^{2+}\)-carboxylate systems, at \(I = 0.1\) mol L\(^{-1}\), with a V-550 Jasco spectrophotometer (optical path 1.000 cm). The solution being examined is transferred from the potentiometric to an optical cell using a peristaltic pump. Due to the low values of molar absorptivity coefficients of vanadyl containing species, the concentration of oxoido cation is always higher than 4 mmol L\(^{-1}\), with the suitable metal to ligand ratio.

2.4 EPR measurements

The EPR spectra of VO\(^{2+}\)-carboxylate systems are recorded in quartz flat cell at room temperature with an ESP-300E Bruker X-band spectrometer. Experimental parameters are as follows: microwave power 4 mW, microwave frequency 9.68 GHz, modulation amplitude 4 Gauss, modulation frequency 100 KHz, time constant 81.92 ms, time sweep 84 s.
To determine all parameters of the electrode system, the titration data of calibration procedure are elaborated using the non-linear least squares computer program ESAB2M [20]. This program allows us to refine the analytical concentration of the reagents, the electrode formal potential $E^0$, the coefficient $j_a$ relative to the acidic junction potential (according to the equation: $E_j = j_a [H^+]$) and the ionic product of water $K_w$; it is also useful to evaluate the purity of the ligand examined.

The refinement of the formation constants is performed by the BSTAC [21] software. It employs an iterative and convergent numerical method, which is based upon the linear combination of the mass balance equations, minimises the error squares sum on electromotive force values and takes into account eventual variations of ionic strength among and/or during titrations. In view of the experimental pH range, the contribution of acidic junction potential is taken into account in the elaboration of data.

Spectrophotometric data were analysed by means of the least squares home-made computer program MOLEX [22] which calculates the values of molar absorptivity coefficients ($\epsilon_\lambda / L \cdot mol^{-1} cm^{-1}$) of the different complexes by using experimental spectra (absorbance vs. wavelength $\lambda$/nm), analytical concentrations of the reagents and the proposed chemical model (stoichiometric coefficients and known stability constant values of all complexes) as input. After the calculation of the species distribution, absorption spectra are estimated for each complex formed in solution, only assuming the additivity of the absorbance in the investigated concentration range. Neither assumptions on the shape of the curves nor on the nature of electronic transitions are taken into account by the program.

The vanadyl complexes spectra are characterized by more than one absorption bands, whose exact
position is identified by a Gaussian deconvolution by means a data analysis software (Origin 6.1). EPR spectra of VO$^{2+}$ solutions show typical unequal spacing between the lines due to second order effects. Therefore, in order to obtain the correct values of $g$ and $A$, experimental data are analysed with the EPR simulation program SIM32, written by T. Spałek and Z. Sojka [23, 24]. All the DFT computations have been performed with the Gaussian09 package [25], using the standard tight convergence criteria. Details about the functional and basis set employed are reported in the DFT calculation paragraph.

3. Results

3.1 EPR spectra

EPR spectra of VO$^{2+}$-malate/tartrate solutions, at different pH, are recorded at room temperature in the same conditions of the potentiometric measurements. At very low pH values, EPR spectra show the typical eight lines pattern of vanadyl mononuclear complexes, due to the coupling of the unpaired electron with $^{51}$V nucleus ($S = 1/2, I = 7/2$). With increasing pH, the values of the isotropic hyperfine coupling constant $A_0$ decrease, revealing the progressive substitution of the water molecules in the [VO(H$_2$O)$_4$]$^{2+}$ aquoion with one or more ligand donor groups. At the same time, the intensity of each EPR spectrum also decreases. The progressive disappearance of the EPR signals is attributable to the formation of magnetically coupled dinuclear species, but a different behaviour is observed for the two ligands. In the case of VO$^{2+}$-L-malate complexes, the dinuclear species are EPR silent ($S = 0$), due to an antiferromagnetic exchange interaction which occurs when two vanadyl groups have coplanarity of their $d_{xy}$ orbitals [26]. At pH 5.5, for solutions with metal to
ligand ratio of 1, the overall spectrum intensity is reduced at approximately 16% of the starting one, and only one species with $A_0 = 97.45 \times 10^{-4} \text{ cm}^{-1}$ is observable. The experimental spectra are reported in the Supplementary material (Appendix A), Fig. S3. On the basis of the additivity method [27,28], this spectrum can be ascribed to a mononuclear complex where VO$^{2+}$ is coordinated by one –COO$^-$, one OH$^-$ and two water molecules. As for the VO$^{2+}$ solutions in the presence of an excess of malate, the decrease of intensity of the EPR spectra with increasing pH is less evident. At low pH values two sets of signals can be observed (Fig. 4). These EPR patterns show different $A_0$ values, 102.10 $\times 10^{-4} \text{ cm}^{-1}$ and 92.70 $\times 10^{-4} \text{ cm}^{-1}$ respectively. On the basis of the additivity method [27,28], the first one can be assigned to a species where the VO$^{2+}$ is coordinated by two –COO$^-$, and two water molecules, probably with stoichiometry [VO(mal)]$^0$, and the second one to a species where the VO$^{2+}$ is coordinated by two –COO$^-$, one R-O$^-$ and one water molecule. As pH increases, these species progressively disappear until, at pH 7.5, the total intensity of the EPR spectrum is only 30% of the initial one. At this pH, the species with $A_0 = 92.70 \times 10^{-4} \text{ cm}^{-1}$ is still present and a new species with $A_0 = 82.30 \times 10^{-4} \text{ cm}^{-1}$ can be observed. On the basis of the additivity method [27,28], the latter can be ascribed to a complex where the donor groups are two carboxylate and two R-O$^-$ groups, probably with a stoichiometry [VO(mal)$_2$H$_2$]$^4$. As for the VO$^{2+}$-L-tartrate complexes, the formation of dinuclear - EPR silent - species is also evident at very low pH values (Supplementary material, Fig. S4). In addition, starting from pH 4, the progressive disappearing of all the mononuclear species reveals the presence of a very low percentage (< 1%) of a complex attributable to a not-silent dimer in triplet state ($S = 1$) (Fig. 5), deriving from a ferromagnetic coupling already described for VO$^{2+}$-L-tartrate system [11,23]. Further, only in the presence of an excess of ligand, a mononuclear species with $A_0 = 82.30 \times 10^{-4} \text{ cm}^{-1}$, similar to that observed in the case of the VO$^{2+}$-L-malate complex, can be observed at pH 6.3 with a percentage of formation of approximately 5-7%.
3.2 Analysis of potentiometric data and speciation models

The potentiometric data recorded before pH 7 are elaborated in order to obtain the speciation model and the stability constant of the complexes. For pH values higher than 7, even with high excess of ligand, equilibrium conditions cannot be reached because of precipitation or oxidation of vanadium(IV) to vanadium(V). The instability of vanadium(IV) solutions was observed with all the experimental techniques utilized. The results of the elaboration are reported in Table 1, with protonation constants of the ligands and statistical parameters of the fits. Calculations were performed by considering the formation of hydrolytic species of the oxido cation, \([\text{VO(OH)}]^+\) and \([\text{(VO)}_2(\text{OH})_2]^{2+}\), the formation of the ion pairs vanadyl–sulphate and vanadyl–chloride, and the protonation of sulphate anion. The formation constants of these species are reported in ref. 2 and 31 (\(\log \beta_{\text{VO(OH)}} = -5.78\) and \(\log \beta_{\text{(VO)}_2(\text{OH})_2} = -6.94\); for sulphate \(H\beta = 1.54\) and \(\log \beta_{\text{VO(SO}_4)} = 1.80\); \(\log \beta_{\text{VOCl}} = 0.04\)). The formation constants of hydrolytic species were calculated from titration data of vanadyl solutions before precipitation of solid phase, but in presence of ligand, it is possible to work at higher pH with respect to solution with oxido cation only, therefore we tested the formation of \([\text{(VO)}_2(\text{OH})_3]^-\) and \([\text{VO(OH)}_3]^-\) [16,32]. Even if for \([\text{(VO)}_2(\text{OH})_3]^-\) we obtained a formation constant (\(\log \beta_{\text{(VO)}_2(\text{OH})_5} = -19.76\pm0.09\)) higher than that of ref. 32 (\(\log \beta_{\text{(VO)}_2(\text{OH})_5} = -22.0\)), the percentage of formation of this species, in our experimental conditions, is negligible, while the formation of the less important species \([\text{VO(OH)}_3]^-\) was excluded by the elaboration process. The percentage of formation of \(\text{VOCl}^+\) is negligible, also.

The speciation models for both the vanadyl/ligand systems have been elaborated from potentiometric data, but taking into account the whole of experimental information. In the tartrate system the potentiometric data lead to chemical models unambiguous and coherent with
spectroscopic results, while, for malate system the selection of the speciation model have been found to be more difficult. The potentiometric data can be explained with more than one chemical model and only taking into account the EPR and UV-vis results it is possible to provide an accurate data interpretation. The species distribution diagrams resultant from the speciation models proposed are shown in Figs. 1 and 2. For both the systems we propose the formation of mononuclear, VOLH and VOL$_2$H$_n$, dinuclear (VO)$_2$L$_2$H$_n$ and binuclear (VO)$_2$LH$_n$ species. The term H$_n$ means that the complexation reaction gives more protons than the acidic ones coming from the ligand molecule (i.e. from alcoholic groups or hydrolysis). L-malate also forms VOL species, while with L-tartrate, due to the formation of dinuclear complexes at low pH values, this species is negligible. It is highly probable that both malate and tartrate form dinuclear complexes with the participation of deprotonated alcoholic groups in the coordination in agreement with the progressive disappearance of the EPR signals attributable to the formation of magnetically coupled dinuclear species. According to the literature data [17], the formation of a mononuclear VOLH$_{-1}$ complex of malate was reported without any hint to an eventual presence of dimers. We tried to explain the experimental data by considering a chemical model involving both dinuclear and mononuclear deprotonated species and the best fit is consistent with the formation of predominant dinuclear species ((VO)$_2$L$_2$H$_{-1}$, (VO)$_2$L$_2$H$_{-2}$ and (VO)$_2$L$_2$H$_{-3}$) and an unimportant concentration of mononuclear VOLH$_{-1}$. The presence of the species [VOmalH$_{-1}$] could be neglected on the basis of the potentiometric titrations only, but the EPR spectra recorded at pH 5.5, for solutions with metal to ligand ratio of 1, reveal the presence of a mononuclear species in the solutions, as reported above. This experimental evidence cannot be ignored, and the [VOmalH$_{-1}$] is the only species that fits with potentiometric data and is coherent with a value of $A_0 = 97.45 \times 10^{-4}$ cm$^{-1}$. The speciation models proposed are in accordance with EPR signals, not only with respect to the nature of the species, but also with respect to the quantity. The decrease of the spectrum intensity at 15% of the starting one,
for solutions with VO\textsuperscript{2+}/malate = 1, at pH 5.5, is coherent with the VO\textsuperscript{2+} percentage involved in the VOLH\textsubscript{1} calculated with the chemical model (Fig. 1a). At this pH only this species gives EPR signal.

As regards the dinuclear complexes of tartrate, our model shows that they are quite predominant in solution over a wide range of pH (the (VO)\textsubscript{2}L\textsubscript{2}H\textsubscript{1} species is already present at pH 2) in accordance with the low intensity of EPR signals recorded (Supplementary material, Fig. S4). The formation of dimers is much favoured by the presence in the ligand molecule of hydroxyl groups which can coordinate VO\textsuperscript{2+}, both in the protonated and deprotonated form. Even in excess of ligand (C\textsubscript{L}:C\textsubscript{VO} = 40:6) the formation of complexes with a ratio tar/VO = 2 is not very significant. Up to pH 7, Lodyga-Chruscinska et al. [16], working with ligand to metal ratios up to 10:1, found the formation of the relevant complex [VO(tar)\textsubscript{2}H\textsubscript{2}]\textsuperscript{4-}. With excess of tartrate, this species is consistent with our speciation model as well, but its formation percentage is less than 10%. No evidence is obtained for the formation of [VO(tar)\textsubscript{2}H\textsubscript{3}]\textsuperscript{5-} and [VO(tar)\textsubscript{2}H\textsubscript{4}]\textsuperscript{6-}, which according to Lodyga-Chruscinska et al. [16] are formed at pH values > 9 (as outlined before, we are not able to obtain equilibrium conditions above pH 7).

The complexes with stoichiometry MLH is formed by the coordination of a carboxylate group to the oxido cation, but the stability constants of these species, even if subtracting the contribution due to the carboxylate protonation, is higher than that of acetate (logK\textsubscript{ML} = 1.81) [1]. The values of logK for MLH complexes (logK is referred to the reaction VO\textsuperscript{2+} + H\textsubscript{r}L\textsuperscript{r–z} ⇌ VOH\textsubscript{r}L\textsuperscript{2+r–z}, with z = charge of the fully deprotonated ligand) reported in Table 1 for L-malate and L-tartrate, might suggest the involvement of a second donor group in the coordination. A similar behaviour was previously recorded for malonate [1] and the participation of the protonated carboxylic group in the coordination has been proposed. The species with stoichiometry VOL of L-malate can involve a seven membered chelate ring due to the coordination of two carboxylate donors, but the logK\textsubscript{ML} of
4.85 is higher than that of succinic acid ($\log K_{ML} = 3.25$) [1]. The hydroxyl group involvement seems to be probable as just reported for other hydroxoacids [2].

3.3 Visible spectra

The visible spectrophotometric measurements have been performed at different pH values, in the same experimental conditions as potentiometric ones. Experimental spectra of vanadyl with L-malate and L-tartrate are reported in Fig. 3. Both the ligands originate binary systems with show the presence of three absorption bands in the acidic pH-range. The first one (I) in the range 820–750 nm, the second one (II) in the range 600–550 nm and the third one (III) in the range 400–430 nm. The increasing of pH provides a clear ipo- and batho-chromic effect of the band I, an intense increasing of absorption values of the band II and the clear appearance of the band III. For pH higher than ~6 the systems present spectra with four absorption bands, with maxima absorption values at about 400, 530, 595 and 850-900 nm. For each system investigated, from the whole of the spectra recorded on solutions at different concentrations and pH values, we have also estimated the individual spectrum of the relevant species in solution. The principal spectral features of these complexes are listed in Table 2 and the spectra are reported in Figs. S1-S2 of Supplementary material (Appendix A). For each complex the values of $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ of the bands are identified through a Gaussian deconvolution in order to better locate the band position when the spectrum presents a shoulder instead of a well-defined maximum. For pH higher than ~6 the model speciation assumes, for the malate system, the increase of the species $[\text{VO(mal)}_2\text{H}_2]^+$ and $[(\text{VO})_2(\text{mal})_2\text{H}_3]^{3-}$, and the increase of $[(\text{VO})_2(\text{tar})_2\text{H}_4]^{4-}$, in the case of tartrate (see Figs. 1, 2). The software elaboration ascribes a calculated spectrum with four absorption bands to $[\text{VO(mal)}_2\text{H}_2]^+$ and to
324 $[(\text{VO})_2(\text{tar})_2\text{H}_4]^4^+$.  

325

326 3.4 DFT calculation

327

328 3.4.1 Set up of the computational method

329

330 The proposed speciation has been checked by means of a computational modelling. Various DFT
331 studies concerning vanadyl coordinated by oxygenated ligands have been reported [16,33,34], and
332 results were obtained by employing different hybrid functional and basis set. We have set up the
333 computational method by examining the well-known aqua-vanadyl complex, both in the form of
334 $[\text{VO(H}_2\text{O})_5]^{2^+}$, with four equatorial and one axial water ligand, and $[\text{VO(H}_2\text{O})_4]^{2^+}$ system, with only
335 equatorial ligands. According to Dos Santos et al. [33] the best balance between exchange and
336 correlation functional has been obtained with the exchange functional of Perdew, Burke and
337 Ernzerhof (PBE) and the gradient-corrected correlation functional of Perdew (P86), with a fine
338 integration grid and . We used the 6-31g basis set for the light elements and the Los Alamos ECP
339 and double zeta basis set (LANL2DZ) for the vanadium. We optimized geometry without symmetry
340 constraints and obtained a minimum, (according to all positive vibrational frequencies) with a $C_{2v}$
341 point group. The geometric parameters agree with the experimental data [35,36] (see Table 3).
342 Vibrational stretching of V=O is computed at 1062 cm$^{-1}$ (unscaled) or 998 cm$^{-1}$ (scaled with the
343 common 0.94 factor) for the penta-aqua complex, and 1091 cm$^{-1}$ (unscaled) or 1025 cm$^{-1}$ (scaled)
344 for the tetra-aqua complex. These values are in good accord with the experimental at 996 cm$^{-1}$ [6].
345 Electronic transition computed by TD-DFT for $[\text{VO(H}_2\text{O})_5]^{2^+}$ are 698 nm (0.0001) ($d_{xy}$ → $d_{xz}$); 630
346 nm (0.0002) ($d_{xy}$ → $d_{yz}$); 522 nm (0.0000) ($d_{xy}$ → $d_{x^2-y^2}$); while the complex $[\text{VO(H}_2\text{O})_4]^{2^+}$ shows
three transition computed at 740 nm (0.0002) \((d_{xy} \rightarrow d_{sz})\); 570 nm\((0.0001)\) \((d_{xy} \rightarrow d_{yz})\); 529 nm \((0.0000)\) \((d_{xy} \rightarrow d_{sz-yz})\). The water complex of VO\(^{2+}\) presents two features, respectively at 765 and 635 nm (spectra reported in the Supplementary material, Fig. S5). Surprisingly, the values computed for \([\text{VO(H}_2\text{O)}_4]^{2+}\) are in better accord with the experimental pattern, notwithstanding many experimental works \([37,38]\) indicate that the common water complex of vanadyl ion is the penta-aqua specie. This suggests to be very careful in the using electronic spectra to validate a modelled species. It is significant the variation of the position and intensity of the bands of the electronic spectrum in the aqua-complexes of VO\(^{2+}\), that indicates a great sensibility of the UV-vis pattern to the coordination sphere. For this reason we have explored the effect of changing the ligand charge, by substitution of H\(_2\)O with OH\(^-\) ion. We analysed various geometries: \([\text{VO(OH)}(\text{H}_2\text{O})_3]^+; \text{cis- and trans-}[\text{VO(OH)}_2(\text{H}_2\text{O})_2]; [\text{VO(OH)}_4]^{2-}\). In Fig. 6 are reported the computed electronic spectra. An exploration of the MO composition shows that the substitution of the water ligand with hydroxide ions modifies the energy of \(d\) orbitals with a consequent alteration of the intensity pattern and position of UV-vis bands. Substitution of two water with OH\(^-\) gives intensity to the high-energy transition at around 450 nm. This result is in accordance with the UV-vis spectra obtained for the hydroxylated acids (see Fig 3). The participation of R-O\(^-\) or OH\(^-\) to vanadyl coordination gives spectra with bands II shifted to lower wavelength and increased intensity with respect to aqua-vanadyl complex (see Table 2).

3.4.2 DFT simulation of the complexes.

For the complexes with stoichiometry M:L = 1:1 of VO\(^{2+}\) with malate, various models can be computed. In Fig. 7 we report two possible geometries for the complex [VOmalH\(_4\)]\(^+\): a complex
with the two –COOH and the –OH all deprotonated and coordinated to the vanadyl ion, and the fourth coordination site occupied by a water molecule, [VOmalH\textsubscript{1}\textsuperscript{-}] - (I); a complex with one –COOH and the –OH, both deprotonated, coordinated to the VO\textsuperscript{2+} ion, and the other two equatorial coordination sites occupied by water molecules, [VOmalH\textsubscript{1}\textsuperscript{-}] - (II). The distortion parameter $\tau$ of the structure [39] (I) is 0.83, close to the value 1.0 typical of trigonal bipyramid arrangement of the oxygen atoms; while for the structure (II) $\tau = 0.15$, revealing a square pyramid arrangement. The interaction with the alcoholic oxygen generates a bond distance shorter than carboxylic oxygen, in accord with the experimental trend found in hydroxyl-carboxylate complexes of vanadyl ion.

Similarly to the mononuclear complex, also for the binuclear complexes (VO)\textsubscript{2}(mal)\textsubscript{2}H\textsubscript{n} of the malate several structures can be proposed. Crystal structures of V(IV) complexed by malic acid are not reported in the CSD (Cambridge Structural Database): there are binuclear species containing V(V) as dioxidovanadium ion [40] or as VO ion equatorially coordinated by a dioxygen ligand [41,42]. Because the recorded electronic spectra are more coherent with a square-pyramidal VO(O)\textsubscript{4} geometry, we have examined (VO)\textsubscript{2}(mal)\textsubscript{2}H\textsubscript{n} models with this arrangement of ligand coordinated to vanadyl ion. The local coordination of the vanadyl ions in this antiorthogonal arrangement has been first analysed with a simpler system, containing only hydroxyl ions coordinated to the vanadium, [(VO)\textsubscript{2}(OH)\textsubscript{6}]\textsuperscript{2-}, four terminal and two bridged (Table 3 and Fig. S6). The electronic spectrum computed for this species is in good accord with the pattern found for the vanadyl-malate systems, (see Supplementary material, Appendix A) both for the wavelength than for the intensities of the bands. In Fig. 8-Ia we report the optimized geometries for a complex showing the malic acid fully deprotonated, coordinated by one carboxylic and two hydroxylic oxygen. The fourth equatorial coordination site of the vanadyl is occupied by a water molecule. The two vanadyl ions are arranged in an antiparallel way, and the system is diamagnetic. The mean distortion parameter $\tau$ is 0.1 and
the coordination geometry of vanadium is closer to the square pyramid. The different protonation of the oxygen in the fourth coordination site of the vanadyl induces appreciable changes in the geometric parameter of the other coordinated oxygen, and this involves significant changes on the electronic spectra (see Supplementary material, Appendix A). A complex containing two malate coordinated by means of both carboxylate groups and the hydroxyl oxygen is reported in the Fig. 8-Ib. This complex shows a significant deviation of the V=O orientation from the anti-parallel disposition of the systems previously examined; the O-V-V angles are respectively 130 and 94 degrees, and this make the complex paramagnetic. The τ factor for both the vanadyl ions is 0.03, so the local geometry is very close to that pyramidal, with a trapezoidal base because of the O···O distance shorter in the hydroxyl groups than in the carboxyl. The computed electronic spectra show the three bands clearly shifted from the experimental ones (see Supplementary material, Appendix A). The dinuclear complex can be competitive with the formation of a mononuclear species, [VO(mal)$_2$H$_2$]$_2^+$. For this reason we have analysed the free energy variation for the reactions:

1) \[ 2[VO(OH_2)_5]^{2+} + 2\text{mal}^{2-} \rightleftharpoons [(VO)_2(malH_1)_2]^{2-} + 2\text{H}_3\text{O}^+ + 8\text{H}_2\text{O} \]

2) \[ [VO(OH_2)_5]^{2+} + 2\text{mal}^{2-} \rightleftharpoons [(VO)(malH_1)_2]^{4+} + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} \]

malH$_1$ is the malic acid with the two –COOH and the –OH groups deprotonated. We have employed structures optimized to a minimum of energy, and considering the water solvent effect by using the PCM model. For reaction 1) we obtained \( \Delta G = -35 \) kJ/mol, and for reaction 2) \( \Delta G = 190 \) kJ/mol. The [(VO)$_2$(mal)$_2$H$_2$]$_2^+$ structure seems therefore the more favoured. Another possible coordination geometry for dinuclear complexes is that found in tartrate binuclear systems. Crystal structures of different dinuclear complexes M$_2$L$_2$H$_n$ have been reported [43,44], and the coordination to vanadyl ion involves the oxygen of the two hydroxyl and two carboxyl deprotonated...
groups. Tapscott reports also that the optical spectra of solid complex is similar to that in solution and proposes that the complex maintains the same structure. For this reason we have explored this kind of arrangement for the tartrate and malate ligands (see Table 3 and Figs. 8-Ic and II). The optimized geometries for \([\text{VO}_2(\text{tart})_2\text{H}_4]^4-\) show bond parameters in reasonable accord with experimental data; the O-VO-O angles are sharper, because of the greater computed distance of vanadyl groups (V···V is 4.491 Å (DFT) vs. 3.985 Å). Also in this case the dinuclear complex can be competitive with the formation of a mononuclear species, \([\text{VO}(\text{tar})_2\text{H}_2]^4-\). For this reason we have analysed the free energy variation for the reactions:

1) \[2[\text{VO(OH}_2]_2^{2+} + 2\text{tar}^2- \rightleftharpoons [((\text{VO})(\text{tarH}_2)_2]^4+ + 4\text{H}_3\text{O}^+ + 6\text{H}_2\text{O}\]

2) \[[\text{VO(OH}_2]_2^{2+} + 2\text{tar}^2- \rightleftharpoons [((\text{VO})(\text{tarH}_1)_2]^4+ + 2\text{H}_3\text{O}^+ + 3\text{H}_2\text{O}\]

Also in this case we have employed structures optimized to a minimum of energy, considering the water solvent effect by using the PCM model. For reaction 1) we obtained \(\Delta G = -446\) kJ/mol, and for reaction 2) \(\Delta G = -183\) kJ/mol. The \([\text{VO}_2(\text{tart})_2\text{H}_4]^4-\) structure seems therefore the more favoured.

4. Discussion on the structure of complexes

4.1 Discussion of visible spectra

The experimental spectra are in accordance with previous works dealing with vanadyl-tartrate and -malate systems [3,5,9,13,16,18] and the presence of four bands for the complexes \(\text{M}L_2\text{H}_2\) of
malate, an α-hydroxylated acid, is expected [45,46]. In the case of tartrate systems, some researchers [7,13,16] associated the spectra with four absorption bands only to mononuclear species ML$_2$H$_n$, but this assignment is not fully compatible with our experimental data that clearly proved that the dinuclear species are dominant also at high level of ligand concentration. The low percentage of the species ML$_2$H$_2$ of tartrate, proved both by potentiometric and EPR measurements, cannot explain the experimental spectra (see Figs. 2 and 3). It is reasonable to suppose that also the dimer [(VO$_2$)$_2$(tart)$_2$H$_4$]$^{4-}$ can show a spectra with four absorption bands, given that the tartrate molecule has two α-hydroxylated units and in this complex each vanadyl unit is coordinated by two (O$^-$, COO$^-$) donor sets, likewise in ML$_2$H$_2$ of α-hydroxylated acids. This structure is in accordance with that proposed by Tapscott et al. [43] in the solid state.

The three bands I, II and III of vanadyl spectra can be assigned to $d_{xy} \rightarrow (d_{xz}, d_{yz})$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions, respectively, according to the energy levels scheme generally admitted for oxidovanadium(IV) compounds with square-pyramidal geometry [4,47-49]. Therefore, the spectra of the species MLH, ML and M$_2$L$_2$H$_n$ of L-malate, M$_2$L$_2$H$_1$ and M$_2$L$_2$H$_2$ of L-tartrate and of M$_2$LH$_n$ for both the ligands, were interpreted as done for a square-pyramidal [7,16] complexes, similarly for the complexes of the most of carboxylic ligands [1,2,7,50] and according to the DFT structures (Fig. 8 Ia-c). The presence of four absorption bands is indicative of a change of the geometry around the vanadium centre, strongly distorted towards the trigonal bipyramid, that leads to the splitting of the $d_{xz}$ and $d_{yz}$ levels [7,13,16]. Therefore, the data suggests a geometry strongly distorted towards the trigonal bipyramid for the species ML$_2$H$_2$ of malate, and the M$_2$L$_2$H$_4$ of tartrate.

It is interesting the comparison of these spectra with those of citrate complexes. In our previous paper [2] we illustrated the spectra of the vanadyl-citrate complexes with two absorption bands, but
in view of new results we propose now another spectra interpretation. In Table 2 we report the
spectra of citrate complexes with three absorption bands, where the band II is resolved in two
bands, coherently with level diagrams interpretation and with the asymmetry of spectra contour.
With this ligand the spectra indicate a trigonal distortion for all the species with stoichiometry ML
or M$_2$L$_2$H$_n$ and an increase of the energy associated to the transition $d_{xy} \rightarrow d_{xz}$ (see $-3D_s + 5Dt$
values). This behaviour is different from that of malate and tartrate complexes and could be
explained with the energy levels scheme proposed by Micera et al. [45] for ligands different from
$\alpha$-hydroxycarboxylic acid and which form chelated rings with 6 terms.

4.2 Discussion of EPR spectra

The EPR provides information about the reciprocal plans position of $d_{xy}$ orbitals of the two VO$^{2+}$ in
dinuclear species and, for both vanadyl-ligand systems, gives information about the donor groups
involved in the coordination sphere. The values of $A_0$ have been interpreted on the basis of the
additivity method [27,28] and the stoichiometry of each species, proposed on the basis of this
interpretation, fit very well with the model speciation. Nevertheless, it is necessary to take into
account the possible effect of the trigonal distortion. For example, for mononuclear species, on the
basis of the additivity method [27,28], the $A_0 = 97.45 \times 10^{-4}$ cm$^{-1}$ observed in the EPR spectra of
malate system could be attributable to a [VOmalH$_{-1}$]$^-$ species, where VO$^{2+}$ ion is coordinated by two
water molecule, one carboxylate group and one OH$^-$ ion. Otherwise, taking into account the
structures proposed by DFT calculations (Fig. 7), when all the donor group of malate participate to
the coordination, [VO(mal)H$_{-1}$]$^-$ (I), the trigonal-bipyramidal arrangement ($\tau = 0.83$) induces a
different interaction between the ligands orbitals and the vanadyl group, making unsuitable the
The additivity method [27,28] proposed for planar structures [28]. Therefore, is not possible the attribution of a certain structure to this species on the basis of the experimental data. Whereas much less questionable are the structures of ML or ML$_2$H$_2$, where the coordination by a (COO$^-$, COO$^-$) donor set or by two (COO$^-$, O$^-$) donor sets, respectively, is highly probable.

**5. Conclusions**

The formation percentages of the complexes, calculated applying the chemical model (see Figs. 1b and 2b), are really coherent with the EPR spectra intensity recorded with analogue solutions. The agreement between the speciation distribution (Figs. 1-2) and the nature and the intensity of EPR spectra, for each pH value, confirms the actuality of the chemical model proposed, where the dinuclear species M$_2$L$_2$H$_n$ are predominant for both vanadyl-ligand systems, also in case of high ligand excess. The close combination of speciation studies and spectroscopic characterization led us to obtain an accurate picture of the VO$^{2+}$ behaviour with hydroxylated carboxylic ligands and to propose an improved speciation model, suitable for a wide range of metal to ligand ratio.

On the basis of speciation model and UV-vis spectra obtained for the systems of oxidovanadium(IV) with malate, tartrate and citrate, a spectral behaviour of the oxido cation with hydroxylated carboxylic ligands was proposed suggesting that different spectral effects can occur when the oxido cation is inserted in chelated rings with 6 or 5 terms. Nevertheless, this hypothesis need further study in order to be proved.
Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://

References


[22] A. Sabatini, A. Vacca, Personal communication.


[37] N. M. Atherton and J. F. Shackleton, Proton ENDOR of VO(H$_2$O)$_5$$^{2+}$ in Mg(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O, Mol. Phys., 39 (1980) 1471-1485.


**Figures**

**Fig. 1** Distribution diagrams of vanadyl-L-malate system for solution: a) $C_{VO} = 5.0$ mmol L$^{-1}$, $C_L = 5.3$ mmol L$^{-1}$; b) $C_{VO} = 5.0$ mmol L$^{-1}$, $C_L = 50.0$ mmol L$^{-1}$; $I = 0.1$ mol L$^{-1}$ (KCl) and $t = 25$ °C.

**Fig. 2** Distribution diagrams of vanadyl-L-tartrate system for solutions: a) $C_{VO} = 5.0$ mmol L$^{-1}$, $C_L = 5.33$ mmol L$^{-1}$ in KCl 0.1 mol L$^{-1}$; b) $C_{VO} = 6.0$ mmol L$^{-1}$, $C_L = 40.0$ mmol L$^{-1}$ in NaCl 0.1 mol L$^{-1}$; $t = 25$ °C.
Fig. 3 Experimental visible spectra in function of pH condition of: a) $C_{\text{VO}} = 6 \text{ mmol L}^{-1}$ and $C_{\text{mal}} = 60 \text{ mmol L}^{-1}$ solution; b) $C_{\text{VO}} = 6 \text{ mmol L}^{-1}$ and $C_{\text{tar}} = 40 \text{ mmol L}^{-1}$ solution; $I = 0.1 \text{ mol L}^{-1}$ with KCl (or NaCl for solution a) and $t = 25 ^\circ \text{C}$. The pH values of solutions are reported on each spectrum.
Fig. 4 EPR spectra of VO\(^{2+}\)-malate solutions with \(C_{\text{VO}} = 5.0 \text{ mmol L}^{-1}\) and \(C_{\text{L}} = 50.0 \text{ mmol L}^{-1}\) at different pH values and room temperature. The lines belonging to the different species are labelled as follows: 

- \#, \(A_0 = 102.10 \times 10^{-4} \text{ cm}^{-1}\); 
- §, \(A_0 = 92.70 \times 10^{-4} \text{ cm}^{-1}\); 
- *, \(A_0 = 82.30 \times 10^{-4} \text{ cm}^{-1}\).
Fig. 5 EPR spectra of VO$^{2+}$-tartrate solutions at room temperature. Signals of: a) mononuclear species recorded at pH 6.3 with $C_{VO} = 6.0$ mmol L$^{-1}$, $C_L = 40.0$ mmol L$^{-1}$; b) dinuclear species ($S = 1$) recorded at pH 4.5 with $C_{VO} = 5.0$ mmol L$^{-1}$, $C_L = 5.0$ mmol L$^{-1}$.

Fig. 6 Computed electronic spectra of [VO(OH)(H$_2$O)$_3$]$^+$; cis- and trans-[VO(OH)$_2$(H$_2$O)$_2$]; [VO(OH)$_4$]$^{2-}$.
**Fig. 7.** The complex $[\text{VOmalH}_4]^{-}$, form (I), left; form (II), right.

**Fig. 8.** Possible structures of the complex: Ia-c) $[(\text{VO})_2(\text{mal})_2\text{H}_2]^{2-}$; II) $[(\text{VO})_2(\text{tart})_2\text{H}_4]^{4+}$. 
Table 1 Protonation constants of carboxylic acids and formation constants for VO\(^{2+}\)-carboxylate systems, at \(I = 0.1\) mol L\(^{-1}\) (KCl) and \(t = 25^\circ\)C.

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<th>Ligand</th>
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<th>(\log \beta_{\text{pp}}^{\text{a}})</th>
<th>(\log K^{\text{b}})</th>
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<td>VOL</td>
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<td></td>
<td>VOLH(_1)</td>
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\(^{a}\) refer to the general reaction: \(p\text{VO}^{2+} + q\text{L}^- + r\text{H}^+ \rightleftharpoons (\text{VO})_p\text{L}_q\text{H}_r^{2p+q}\)

\(^{b}\) \(\log K\) values are calculated from \(\log \beta\) values and refer to the reaction: \(p\text{VO}^{2+} + (2p-r)\text{L}^- = (\text{VO})_p\text{H}_r\text{L}^{2p-r}\), with \(z\) = charge of the fully deprotonated ligand

\(^{c}\) ± standard deviation.

\(^{d}\) weight for each experimental point is given as \(w = 1/s^2\) (see ref. 21)

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Table 2 Values of $\lambda_{\text{max}}$/nm, $\varepsilon_{\text{max}}$/dm$^3$ mol$^{-1}$ cm$^{-1}$, -3$D_s$+5$D_t$ (kK) and 10$D_q$ (kK) for relevant species in solution.

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<th>$\varepsilon_{\text{max}}$/dm$^3$ mol$^{-1}$ cm$^{-1}$</th>
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$^a$ The uncertainty on $\varepsilon_{\text{max}}$ values ranges between 1 and 10%.

$^b$ The term -3$D_s$+5$D_t$ correspond to the energy of electronic transition $d_{xy} \rightarrow d_{xz}$, $d_{xy}$ or $d_{yz} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$, and the 10$D_q$ correspond to the energy of $d_{xy} \rightarrow d_{x^2-y^2}$.

$^c$ The transition energy uncertainty is of 0.1 kK units considering that the $\lambda_{\text{max}}$ values are obtained elaborating the experimental absorbance values sampled each 5 nm.

$^d$ sh = shoulder.
Table 3 Structural parameters obtained from DFT calculations for vanadyl complexes in water.

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<td>d(V=O)</td>
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<td>d(V-O)$_{eq}$</td>
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<td>d(V-O)$_{ax}$</td>
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<td>d(V-O)$_{OH}$</td>
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709

710