Oxovanadium(IV) Complexes of Mercaptocarboxylic Acids

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Complex formation between oxovanadium(IV) and a series of aliphatic mercaptocarboxylic acids (mercaptoacetic, 2- and 3-mercaptopropionic, 2-mercaptosuccinic, and *meso*-2,3-dimercaptosuccinic) was studied in aqueous solution by potentiometric and spectroscopic (EPR and electronic absorption) techniques. A comparison with the complexes of the corresponding hydroxycarboxylic acid analogues was also made. The most interesting finding is that VO^{2+} has a similar affinity to the rather soft thiolate-S donors as to the hard alcoholate-O donors, if these donors are in chelatable position with a hard carboxylate group. The bidentate mercaptocarboxylates form (CO_2^-, S^-)-co-ordinated mono and bis complexes, while bis complex formation is rather hindered with the tridentate 2-mercaptosuccinic acid. Due to the high denticity of the ligand, 2,3-dimercaptosuccinic acid readily forms oligomeric species *via* the co-ordination of all potential donor groups.

Owing to the recent evidence for V–S co-ordination in various biomolecules,[1,2] vanadium–sulfur complexes are now of increasing interest. Most papers so far published in this field deal with the preparation of various sulfur-containing complexes whereas relatively little work has been done in solution. From its position in the Periodic Table, one can expect that vanadium forms rather hard cations, the hardness increasing with increasing oxidation state. It is known that oxovanadium(IV) forms strong complexes with hard O-donor ligands, such as carboxylates, hydroxycarboxylates, hydroxamates, salicylates, catecholates, *etc.*[2–10] Much less is known, however, on its complex-forming ability with soft S-donor ligands.[2,11–15] For instance, the results so far reported on the binding of VO^{2+} to the simplest mercaptocarboxylic (mercaptoacetic and 2-mercaptopropionic) acids are rather contradictory. Jacobsen and Strom[11] failed to detect any complex-formation process between mercaptoacetic acid and VO^{2+}, whereas Reeder and Rieger[12] reported EPR evidence for the formation of stable mono and bis complexes with both the above ligands in the acidic pH range. At the same time a recent comparative spectral study[15] on malic and 2-mercaptosuccinic acids, revealed strong similarity in the complex-forming properties of these two ligands with VO^{2+}.

In this paper we present a potentiometric and spectral (EPR and electronic absorption) study on the binding ability of a series of mercaptocarboxylic ligands, namely mercaptoacetic (H_2maa), 2-mercaptopropionic (2-H_2mpa), 3-mercaptopropionic (3-H_2mpa), 2-mercaptosuccinic (H_3msucc) and *meso*-2,3-dimercaptosuccinic (H_4dmsucc) acids, to oxovanadium(IV). A comparison was also made with the complexes of the corresponding hydroxy-analogues, glycolic (hydroxyacetic, Hga), lactic (2-hydroxypropionic, Hlact), malic (2-hydroxysuccinic, H_2mal) and *meso*-tartaric (2,3-dihydroxysuccinic, H_2tart) acids.

Experimental

Reagents.—The ligands used were Aldrich products of puriss quality. The acids 2-H_2mpa, H_3msucc, Hlact and H_2mal were racemic mixtures. Their purity was checked and the exact concentrations of their solutions were determined by the Gran method.[16] The VO^{2+} stock solution was prepared as described[17] and standardized for the metal-ion concentration by permanganate titration and for hydrogen-ion concentration by potentiometry. The ionic strength of all solutions studied was adjusted to 0.2 mol dm^{-3} KCl. In all cases the temperature was 25.0 ± 0.1 °C.

Potentiometric Measurements.—The stability constants of the proton and oxovanadium(IV) complexes of mercaptocarboxylic acids were determined by pH-potentiometric titration of 25 cm^3 samples. The concentration of the ligand was 0.002, 0.004 or 0.008 mol dm^{-3}, and the molar ratio between the metal ion and ligand was 0:2, 1:1, 1:2 or 1:4. The titrations were performed over the range pH 2.2–7, or until precipitation occurred, with KOH solution of known concentrations (*ca.* 0.2 mol dm^{-3}) under a purified argon atmosphere. With almost all ligands, without ligand excess, the samples became opalescent at pH 5, while the solutions remained clear up to pH 7 or even higher up to pH 10 in the case of 2,3-dimercaptosuccinic acid, when the ligand was in an excess. In these pH ranges equilibrium was reached within about 1 min. The reproducibility of the titration curves was within 0.005 pH unit over the whole pH range. The following stability constants (log β) were assumed for the hydroxo complexes of VO^{2+}: $[VO(OH)]^+$ $\log \beta_{1-1} = -5.94$), $[(VO)_2(OH)_2]^{2+}$ ($\log \beta_{2-2} = -6.95$), calculated from the data published by Henry *et al.*[18] using the Davis equation to take into account the different ionic strengths, and $[VO(OH)_3]^-$ ($\log \beta_{1-3} = -18.0$), taken from ref. 19.

The pH was measured with a Radiometer PHM 84 instrument equipped with a GK 2322C combined glass electrode, calibrated for hydrogen-ion concentration according to the procedure of Irving *et al.*[20]

The concentration stability constants, $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$, were calculated with the aid of the computer program PSEQUAD.[21]

Spectroscopic Measurements.—X-Band EPR spectra (9.15 GHz) were recorded at 298 K using a Varian E-9 spectrometer, absorption spectra on a Beckman Acta MIV spectrophotometer. The composition of the samples and the experimental conditions were the same as described for the potentiometric titrations.

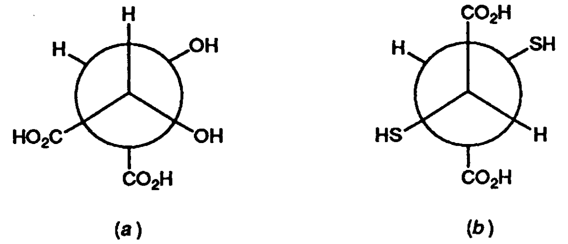
Table 1 Proton (log *K*) and oxovanadium(IV) (log β) stability constants for the complexes of mercaptocarboxylic acids and their hydroxy-analogues at 25.0 ± 0.1 °C and $I = 0.2$ mol dm^{-3} (KCl)

	H_2maa	Hga	2-H_2mpa	Hlact	H_3msucc	H_2mal	H_4dmsucc	H_2tart
log *K* (H_4A)	—	—	—	—	—	—	2.33(1)	—
log *K* (H_3A)	—	—	—	—	3.05(1)	—	3.34(1)	—
log *K* (H_2A)	3.41(1)	—	3.43(1)	—	4.46(1)	3.16(1)	9.45(1)	2.95(1)
log *K* (HA)	10.6	3.58(1)	10.04(2)	3.58(1)	10.17(2)	4.57(1)	11.65(3)	4.43(1)
$VOAH_2$	—	—	—	—	—	—	23.39(3)	—
VOAH	12.8	—	11.85(3)	—	13.51(2)	6.6(2)	20.91(1)	—
VOA	8.6	2.66(2)	8.40(5)	2.79(1)	10.40(1)	4.80(1)	—	4.24(2)
$VOAH_{-1}$	—	−1.35(3)	—	−1.34(3)	4.44(7)	0.85(1)	—	—
$VOAH_{-2}$	—	—	—	—	—	−5.28(2)	—	—
VOA_2H	22.3	—	20.68(8)	—	22.42(8)	—	30.19(12)	—
VOA_2	17.6	4.4(2)	17.55(1)	5.15(5)	17.45(5)	—	20.71(4)	—
VOA_2H_{-1}	—	0.89(7)	—	1.28(6)	—	2.1(4)	—	—
VOA_2H_{-2}	—	−3.98(2)	—	−3.80(3)	—	—	—	—
$V_3O_3A_2$	—	—	—	—	—	—	38.31(11)	—
$V_2O_2A_2$	—	—	—	—	—	—	35.60(1)	—
$V_2O_2A_2H_{-2}$	—	—	—	—	—	—	—	4.05(3)
$V_2O_2A_2H_{-3}$	—	—	—	—	—	—	—	−2.16(5)

Table 2 Basicity-adjusted stability constants for the vanadium(IV) complexes of 2-H_2mpa and some reference compounds

Ligand	Process	log *K*
Acetic acid[a]	$VO^{2+} + HA \rightleftharpoons [VOA]^+ + H^+$	−2.75
Monochloroacetic acid[a]	$VO^{2+} + HA \rightleftharpoons [VOA]^+ + H^+$	−1.62
3-Chloropropionic acid[a]	$VO^{2+} + HA \rightleftharpoons [VOA]^+ + H^+$	−2.35
Lactic acid[b]	$VO^{2+} + HA \rightleftharpoons [VOA]^+ + H^+$	−0.79
2-Mercaptopropionic acid	$VO^{2+} + H_2A \rightleftharpoons [VOAH]^+ + H^+$	−1.81

[a] Ref. 22. [b] Ref. 23.



(*a*) (*b*)

Fig. 1 Proposed preferential conformations in solution: (*a*) *gauche* conformation of *meso*-tartaric acid, (*b*) centrosymmetric *anti* conformation of *meso*-2,3-dimercaptosuccinic acid

Results and Discussion

Protonation constants were calculated from the titration curves of the proton–ligand systems in the range pH 2–11. In the case of mercaptoacetic acid, stable pH-meter readings could not be achieved in the basic pH range, due probably to some decomposition process of the ligand, thus only an approximate protonation constant could be determined for the SH group. Proton and metal complex-formation constants are listed in Table 1 together with some data obtained for the corresponding hydroxy-analogues. Although the titration data in the vanadium(IV)–mercaptoacetate system were reproducible and could be fitted within the experimental error, the metal complex-formation data given in Table 2 can be regarded only as tentative because of the larger uncertainty in the p*K* of the thiol group.

Proton Complexes.—The protonation constants of the carboxylic groups of mercaptoacetic, 2-mercaptopropionic and 2-mercaptosuccinic acids are very similar to those of their hydroxy-analogues (see Table 1). The slightly lower log K_{CO_2H} values observed for the mercapto derivatives can readily be explained by the larger acid-strengthening effect of the thiol group as compared to that of the hydroxyl group, and the lower ability of the thiol group to form hydrogen bonding with the carboxylic function. This relation is more complex for *meso*-2,3-dimercaptosuccinic acid and its hydroxy analogue, *meso*-tartaric acid. As clearly indicated by the data in Table 1, the carboxylic groups of the thiol derivatives are much more acidic. This difference can only be explained if different conformations are assumed for the two ligands. Pettit and Swash[4] concluded that, as in the solid state, *meso*-tartaric acid (and tartrate) exists in solution in a conformation in which the carboxyl and hydroxyl groups are mutually *gauche*. Intramolecular hydrogen bonding of the hydroxyl groups requires their *gauche* disposition. The repulsion between the two negatively charged carboxylate groups of *meso*-tartrate in *gauche* conformation will increase the log *K* values. With the thiol derivative the intramolecular hydrogen bonding between the SH groups is practically negligible, thus the ligand can adopt the sterically most stable centrosymmetric *anti* conformation in which the carboxylate groups are the farthest from each other (see Fig. 1).

For the hydroxy derivatives only carboxylic log *K* values can be measured as the hydroxy groups are not ionized, in the measurable pH range.[4,23] The SH groups of the mercapto derivatives, on the other hand, dissociate in the well measurable range pH 9–11.

Vanadium(IV) *Complexes with Mercaptoacetic and* 2-*Mercaptopropionic Acids.*—It can be seen from the data in Table 1 and the concentration distribution curves in Fig. 2 that both systems could be described by the same speciation model involving 1 : 1 and 1 : 2 (S^-, CO_2^-)-co-ordinated species, [VOA] and $[VOA_2]^{2-}$, respectively, as well as their protonated forms $[VOAH]^+$ and $[VOA_2H]^-$. In the latter two complexes, which are found in relatively low concentration (maximum 10%), carboxylates are assisted by undissociated thiol groups as the ligand donors. This hypothesis is strongly supported by the significantly higher stability of the protonated complexes as compared to the corresponding acetate complex. The basicity-adjusted stability constants, which take into account the

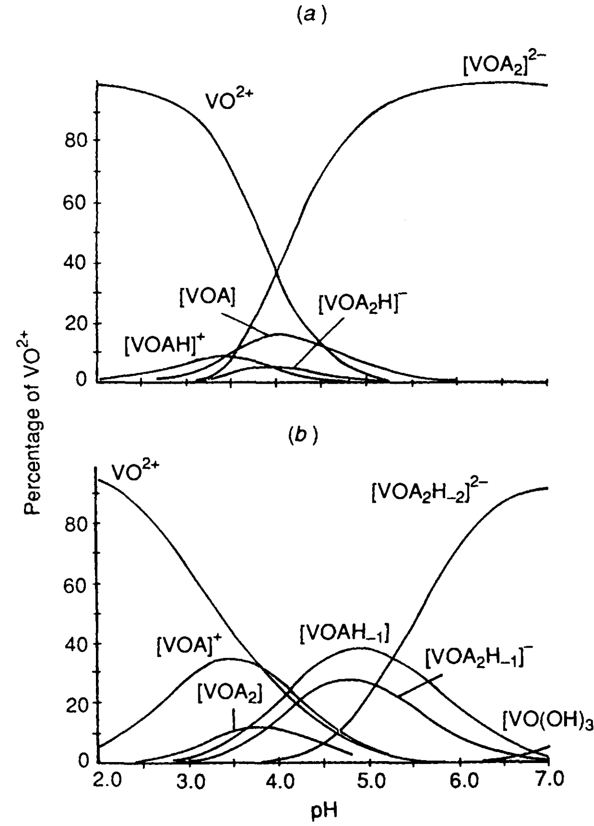


Fig. 2 Speciation curves as a function of pH in the (*a*) vanadium(IV)–2-mercaptopropionic acid and (*b*) vanadium(IV)–lactic acid systems using the constants in Table 1. $c_M = 0.0016$, $c_A = 0.004$ mol dm^{-3}

basicity differences of the co-ordinating donor groups, clearly indicate the stability increase (see Table 2).

When the basicity-adjusted stability constants of the vanadium(IV) complexes of the thiocarboxylates and their hydroxy-analogues are compared in Table 3, it is worthwhile noting that the relative stabilities of the corresponding (S^-, CO_2^-) and (O^-, CO_2^-) co-ordinated complexes do not differ very much. This means that VO^{2+} has a similar affinity for the rather soft thiolate S^- donor to that for the fairly hard alcoholate O^- donor, if these donors are in chelatable position with a hard CO_2^- group. It is also worth noting that the co-ordination of the second thiocarboxylate molecule is much more favoured than the first one because a negative value of $\log(K_{VOA}/K_{VOA_2})$ is observed. This is not unusual for sulfur-containing ligands, as it was observed with other metal ions, like Ni^{II},[24] Zn^{II} and Co^{II}.[25]

The EPR spectral parameters listed in Table 4 substantiate the assignment of the species taking part in complex formation. In accordance with potentiometry, the main species [VOA] and $[VOA_2]^{2-}$, with g_0 and A_0 values suggesting co-ordination of the metal ion to thiolate sulfur and carboxylate oxygen atoms, are distinguished in solution, although microprecipitates are observed with mercaptoacetic acid in the range pH 5.5–12. As these are redissolved above pH 12, the intensity of the signals of the fully hydrolysed species $[VO(OH)_3]^-$ exhibits a steady increase. Higher ligand excesses enhance metal complex formation in solution, which for example is complete at the 100:1 molar ratio, as shown by the total absence of precipitation. Moreover, at these ligand excesses, species involving only carboxylates as the deprotonated donor groups, *e.g.* $[VOAH]^+$, are also observed in very acidic solution (pH *ca.* 1.5), even if they are never unique species. With both ligands, electronic absorption spectra show that the formation of [VOA] complexes results in an intensity increase of the shoulder at 640 nm typical for the aqua ion. The visible spectra of the predominant species $[VOA_2]^{2-}$ consist of two absorption maxima at 570 and 630 nm, respectively. As is usual, a band with a maximum at about 360 nm occurs as the distinctive spectral feature of the hydrolysis process in very basic solution.

On the whole, the above findings are in contradiction with the results of Jacobsen and Strom,[11] who could not detect any complex between VO^{2+} and mercaptoacetic acid in the acidic pH range and proposed co-ordination of VO^{2+} to the oxidized product of the ligand, $HO_2CCH_2SSCH_2CO_2H$. As oxygen was very rigorously excluded under our experimental conditions, we can rule out oxidation of the ligand by air. Further, there was no sign of any redox reaction between VO^{2+} and the ligands, as the complete coincidence of the normal titration curves from pH 2 to 6 and back to 2 supported the reversibility of the reaction. At the same time, the formation of stable complexed species with nine-membered chelated rings, as one can expect for the vanadium(IV)–dithioglycolic acid system, is very unlikely.

Vanadium(IV) *Complexes with* 3-*Mercaptopropionic Acid.*—An examination of the complexing behaviour of 3-mercaptopropionic acid, which is a β-mercaptocarboxylate ligand, can allow the comparison of the stability of six- *versus* five-membered chelation of oxovanadium(IV) by carboxylate and thiolate donors. As judged from spectroscopic measurements, the species formed in this system are remarkably less stable than those with mercaptoacetic and 2-mercaptopropionic acids. At ligand-to-metal molar ratios of 2:1 spectroscopy indicates no significant complex formation because the aqua ion is the only detectable species up to pH 4.0–4.5. As the pH increases the metal ion undergoes hydrolysis and precipitation, as is the case in the absence of ligand. Complexed species are observed in the EPR spectra only at rather high excess of ligand, *e.g.* > 50:1. Under these conditions the metal ion is predominantly bound to carboxylate groups forming 1:1 and 1:2 species [VOA] and $[VOA_2]^{2-}$. The $[VOA_2]^{2-}$ complex exhibits EPR parameters as well as d–d absorption maxima significantly different from those of the analogous α-mercaptocarboxylate species, indicating the sensitivity of these spectroscopies to the ring size around the oxovanadium ion (see Table 4). Then, from pH ≈ 9 the intensity of the EPR signals starts to decrease and vanish almost completely, indicating the formation of polynuclear species with strong exchange interactions between the paramagnetic ions. This complex is presumably a hydroxo-bridged dimer $[(VOAH_{-1})_2]^{2-}$, or more precisely $[\{VOA(OH)\}_2]^{2-}$.

Vanadium(IV) *Complexes with* 2-*Mercaptosuccinic and Malic Acids.*—In principle, the ligand 2-mercaptosuccinic acid can form five-membered (S^-, CO_2^-), six-membered (S^-, CO_2^-), seven-membered (CO_2^-, CO_2^-) chelates and five- + six-membered (CO_2^-, S^-, CO_2) joint chelates with metal ions. However, since the EPR results indicate complex formation between VO^{2+} and 3-mercaptopropionic acid (see above) or succinic acid (see ref. 13) only at very high (> 50:1) ligand molar excess, the formation of the pure six- (S^-, CO_2^-) and seven-membered (CO_2^-, CO_2^-) chelates can be regarded as negligible.

Potentiometric data support the existence of a protonated complex [VOAH] where the ligand is presumably bound in a bidentate (S^-, CO_2^-) manner whereas the terminal CO_2H group is undissociated. As it can be seen in the speciation diagram (Fig. 3), $[VOA]^-$ is the dominant species in the range pH 3.5–5.5. In this complex the ligand is co-ordinated in a terdentate (CO_2^-, S^-, CO_2^-) manner, as supported by the stability constant which is two orders of magnitude higher than those of the $[VOA]^+$ complexes formed with the bidentate lactic or glycolic acids (see Table 1). As the pH is raised, the parallel competitive co-ordination of a hydroxide ion or a second ligand molecule takes place and leads to $[VOAH_{-1}]^{2-}$ and $[VOA_2]^{4-}$, respectively. However, the formation of the bis-chelated complex seems unfavourable, as judged from the rather high $\log(K_{VOA}/K_{VOA_2})$ value, probably due to electro-

Table 3 Derived equilibrium constants for 2-H_2mpa and its hydroxy-analogue Hlact

Ligand	Process	log *K*
2-Mercaptopropionic acid	$VO^{2+} + H_2A \rightleftharpoons [VOA] + 2H^+$	−5.07
	$[VOA] + H_2A \rightleftharpoons [VOA_2]^{2-} + 2H^+$	−4.32
	$\log(K_{VOA}/K_{VOA_2})$	−0.75
Lactic acid *	$VO^{2+} + HA \rightleftharpoons [VOAH_{-1}] + 2H^+$	−4.92
	$[VOAH_{-1}] + HA \rightleftharpoons [VO(AH_{-1})_2]^{2-} + 2H^+$	−6.04
	$\log(K_{VOAH_{-1}}/K_{VOA_2H_{-2}})$	1.28

* Ref. 23.

Table 4 The EPR and electronic absorption parameters of oxovanadium(IV) complexes of mercapto- and hydroxy-carboxylic acid ligands

Ligand	Complex	g_0	$10^4 A_0$/cm^{-1}	Absorption maxima λ_{max}/nm, ε/dm^3 mol^{-1} cm^{-1}
Mercaptoacetic acid	VOAH	1.964	105	
	VOA	1.969	93	
	VOA_2	1.976	81	570 (21) (sh), 630 (28)[a]
2-Mercaptopropionic acid	VOAH	1.965	105	
	VOA	1.968	93	
	VOA_2	1.976	81	570 (26) (sh), 630 (28)[b]
3-Mercaptopropionic acid	VOAH	1.965	104	
	VOA	1.970	93	
	VOA_2	1.976	85	580 (18), 720 (22)[c]
2-Mercaptosuccinic acid	VOAH, VOA	1.973	94	
	VOA_2	1.981	81	555 (33) (sh), 640 (37)[b]
Malic acid	VOA_2H_{-1}	1.970	92	
	$VOAH_{-1}$	1.968	98	
	VOA_2H_{-2}	1.974	82	580 (26) (sh), 830 (27)[b]
meso-2,3-Dimercaptosuccinic acid	$VOAH_2$, VOAH	1.969	93	
	$(VOA)_n$	broad, unresolved spectra		570 (28) (sh), 630 (44)[b]
	VOA_2H_2[d]	1.976	81	570 (36), 630 (46)
	VOA_2[d]	1.983	68	625 (60)

[a] From 5:1 solutions. [b] From 2:1 solutions. [c] From 100:1 solutions. [d] Species observed in solutions at 10:1 A:M molar ratio and not detected by potentiometry. Co-ordination sets: $2(CO_2^-, S^-)$ in VOA_2H_2 and $2(S^-, S^-)$ in VOA_2.

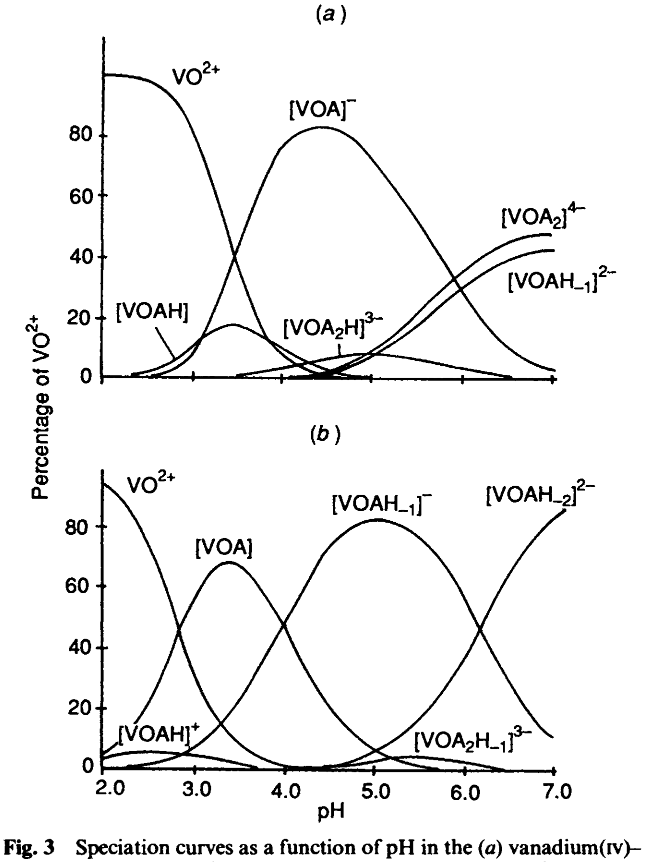


Fig. 3 Speciation curves as a function of pH in the (*a*) vanadium(IV)–2-mercaptosuccinic acid and (*b*) vanadium(IV)–malic acid systems using the constants in Table 1. Concentrations as in Fig. 2

static effects. On the other hand, the calculated pK_{VOA} (= 5.96) is of the same order of magnitude as that of the free aqua ion.

However, EPR spectra show only species with basic chromophores similar to those of simple α-mercaptocarboxylate ligands. This suggests that the in-plane co-ordination of the metal is of the (CO_2^-, S^-) type in both [VOAH] and $[VOA]^-$ species (due to similarity of the EPR parameters, these were previously attributed to bis-chelated carboxylate complexes in ref. 13) and $2(CO_2^-, S^-)$ type in $[VOA_2]^{4-}$, whereas the hydrolysed complex $[VOAH_{-1}]^{2-}$, by undergoing dimer formation, is EPR-silent.

A previous EPR investigation[13] on the vanadium(IV)–malic acid system indicated the presence of three complexed species apart from the simple carboxylate complexes with one or two CO_2^- groups bound to the metal ion. One of these species was assigned as the 1:1 complex involving a terdentate fully ionized molecule (species III in ref. 13), whereas that prevailing above pH 7 exhibited the normal EPR parameters of a basically $2(CO_2^-, O^-)$-co-ordinated species (species IV in ref. 13). Another intermediate species was interpreted as the bis-chelated complex with $2(CO_2^-, CO_2^-)$ co-ordination assisted by an undissociated hydroxyl (species II in ref. 13). A deeper investigation on the complexation of VO^{2+} by α-hydroxycarboxylic acids has now allowed a more reliable interpretation of the structure of this species. Its EPR parameters (g_0 = 1.970, $A_0 = 92 \times 10^{-4}$ cm^{-1}) are very near to those of (CO_2^-, O^-)(CO_2^-, OH)-chelated complexes which may be formed by α-hydroxycarboxylic ligands.[23] A species with similar EPR features is also found in the 2-hydroxy-2-methylbutyric acid (Hhmba)–malic acid–VO^{2+} ternary system at the 1:1:1 molar ratio, while it is absent in the corresponding 1:1 binary systems. On the contrary, an analogous species is not formed in the 1:1:1 succinic acid–malic acid–VO^{2+} and succinic acid–H_2hmba–VO^{2+} systems. These findings suggest that the complex may

Table 5 Derived equilibrium constants for H_3msucc and its hydroxy-analogue H_2mal

Ligand	Process	log *K*
2-Mercaptosuccinic acid	$VO^{2+} + H_3A \rightleftharpoons [VOA]^- + 3H^+$	−7.28
	$[VOA]^- + H_3A \rightleftharpoons [VOA_2]^{4-} + 3H^+$	−10.63
	pK_{VOA}	5.96
	$[VOA]^- + HA^{2-} \rightleftharpoons [VOA_2H]^{3-}$	1.85
	$\log(K_{VOA}/K_{VOA_2})$	3.35
Malic acid	$VO^{2+} + H_2A \rightleftharpoons [VOAH_{-1}]^- + 3H^+$	−6.88
	$[VOAH_{-1}]^- + H_2A \rightleftharpoons [VO(AH_{-1})_2]^{4-} + 3H^+$	—
	$pK_{VOAH_{-1}}$	6.13
	$[VOAH_{-1}]^- + A^{2-} \rightleftharpoons [VOA_2H_{-1}]^{3-}$	1.20

involve two ligands, one of them adopting a joint six- + five-membered chelating mode of the (CO_2^-, OH, CO_2^-) type with a carboxylate group axially bound to vanadium and the other acting as a bidentate (CO_2^-, O^-) donor resulting in a stoichiometry of $[VOA_2H_{-1}]^{3-}$ [see Fig. 3(*b*)]. The same donor arrangement can be achieved if the (CO_2^-, O^-) set belongs to a simple bidentate α-hydroxycarboxylate ligand (*e.g.* Hhmba), whereas it cannot be formed by a pure dicarboxylic acid ligand like succinic acid with either malic acid or Hhmba. At this point we disagree with Vilas Boas and co-workers,[15] who in their very recent publications do not predict high formation probability for 1:2 species with only one co-ordinated alcoholate group. In the species $[VOA_2H_{-1}]^{3-}$ they assume a 2(CO_2^-, O^-) bonding mode in the equatorial plane with a non-co-ordinated protonated carboxylic group. This would lead, however, to a dramatic decrease in the acidity of this carboxylic acid ($pK_{VOA_2H} = 7.0 \pm 0.4$) as compared to that of the free ligand ($pK_{HA} = 4.57$), which cannot be explained easily. Thus we feel that both the spectral and potentiometric data confirm the (CO_2^-, O^-)(CO_2^-, OH) equatorial bonding mode with one non-co-ordinated and one axially co-ordinated carboxylate group, rather than the one suggested by Vilas Boas and co-workers.[15]

Potentiometric data show similar basicity-adjusted stability constants for the corresponding complexes. The only difference is the even less favoured formation of the bis complex in the vanadium(IV)–malic acid system due to the great difference in the acidity of the SH and OH groups.

Vanadium(IV) *Complexes with* meso-2,3-*Dimercaptosuccinic Acid*.—This ligand is the dithio analogue of tartaric acid. The EPR spectra show this ligand to follow a very different complexation scheme to that of simple mercaptocarboxylic acids. Almost independently of the metal ion-to-ligand ratio, the EPR spectra indicate the formation of a main species in acidic solution up to pH 4.0–4.5. The metal co-ordination in this species is analogous to that of the monochelated α-mercaptocarboxylate complexes. At higher pH, apart from the presence of signals due to minor species which may be assigned to 2(CO_2^-, S^-) co-ordination, the EPR spectra are dominated by a rather broad band ($g \approx 2$) lacking hyperfine structure. The resonance gains intensity with decreasing ligand-to-metal ratio and, even more, in spectra recorded in frozen solution. All these observations suggest that the broad EPR signal is the effect of magnetic interactions, mainly of dipolar origin, between vicinal VO^{2+} ions, analogously to solid-state paramagnetic complexes. These spectral features remain unchanged until pH 12, beyond which the magnetically dilute $[VO(OH)_3]^-$ species is detected.

The pH-metric titration data could be fitted well by di- and mono-protonated 1:1 complexes $[VOAH_2]$ and $[VOAH]^-$, and above pH 5, equally well by the formation of either a monomeric $[VOA]^{2-}$, dimeric $[(VO)_2A_2]^{4-}$ or even a trimeric $[(VO)_3A_3]^{6-}$ species. However, when these three species were assumed and refined simultaneously in the pH-metric calculation, the former was always rejected by the computer program. At pH > 9 the formation of bis complexes $[VOA_2H]^{5-}$ and $[VOA_2]^{6-}$ was also detected.

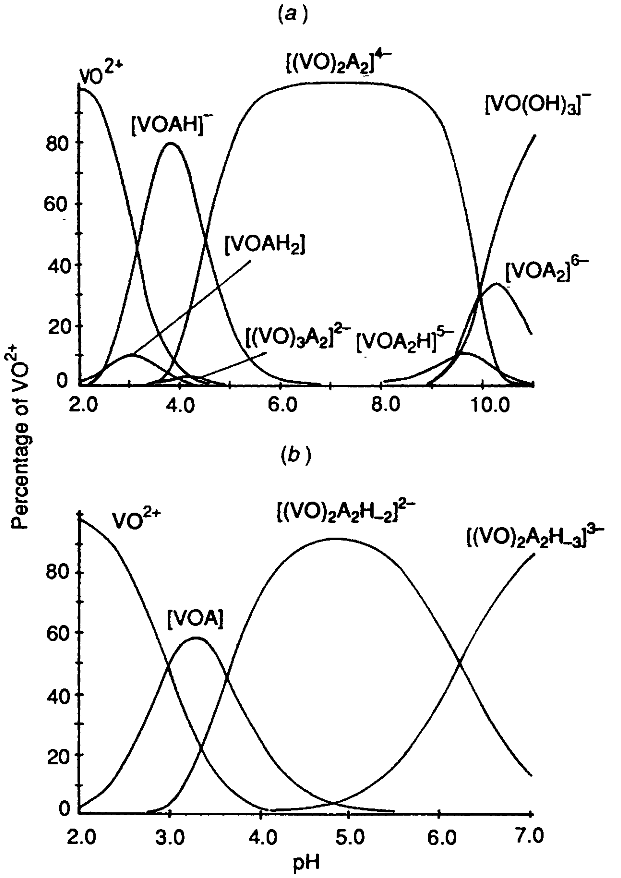
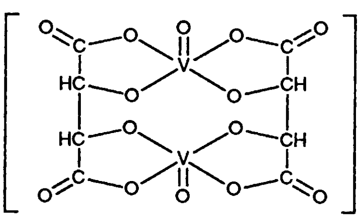


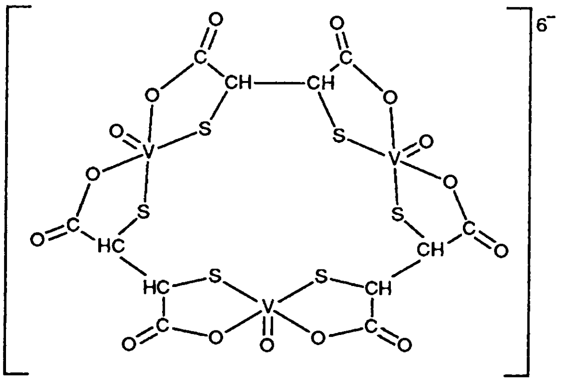
Fig. 4 Speciation curves as a function of pH in the (*a*) vanadium(IV)–*meso*-2,3-dimercaptosuccinic acid and (*b*) vanadium(IV)–*meso*-tartaric acid systems using the constants in Table 1. Concentrations as in Fig. 2

By combining potentiometric and EPR information it is reasonable to assume that the co-ordination of this ligand starts at the α-mercaptoacetate site of the molecule resulting in monochelated species. The other half of the molecule remains fully protonated in $[VOAH_2]$ and partly protonated at the more basic thiol group in $[VOAH]^-$. The similar basicity-adjusted formation constants for the $[VOAH]^-$ species of 2,3-dimercaptosuccinic acid ($\log K = -5.86$ for the process $VO^{2+} + H_4A \rightleftharpoons [VOAH]^- + 3H^+$) and for the $[VOA]^-$ complex of 2-mercaptosuccinic acid ($\log K = -7.28$ for the process $VO^{2+} + H_3A \rightleftharpoons [VOA]^- + 3H^+$) allow the assumption of similar (CO_2^-, S^-, CO_2^-) co-ordination in both complexes.

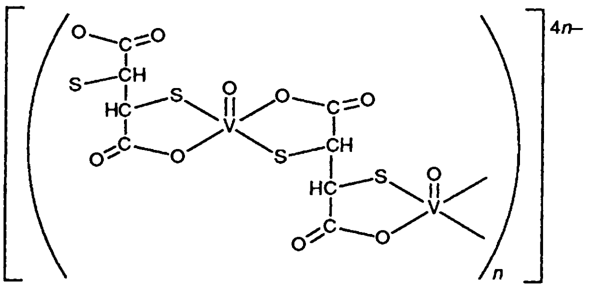
Concerning the nature of the $[(VO)_2A_2]^{4-}$ species of *meso*-2,3-dimercaptosuccinic acid, because the dissociation of the



I



II



III

second thiol group cannot occur at pH values as low as 5.5–6 without co-ordination to the metal, it may be assumed that the four donor atoms of the ligand are all involved in metal binding. To assign the structure of this species, some stereochemical considerations, together with a comparative analysis of the analogous complexes of tartaric acid, were necessary. Tartaric acid forms various dimers in the acidic pH range.[4] It was found that dimers with $[(VO)_2A_2H_{-4}]^{4-}$ stoichiometry are the preponderant species above pH 6 with optically active or racemic tartrates. As confirmed by X-ray diffraction and spectroscopic studies, in these species two VO^{2+} ions, each co-ordinated to one end of both the ligand molecules, link two tartrate(4−) ligands together (see structure **I**) yielding a dinuclear 'cage structure' with a metal–metal distance of 5–6 Å.[5,26,27] In such a case, due to the magnetic interaction of the unpaired electron with two equivalent vanadium nuclei, a typical fifteen-line structure, with a hyperfine constant about one half that expected for an analogous monomeric species, may be observed in the isotropic EPR spectra and a zero-field splitting can be measured in the anisotropic spectra. In contrast, with the *meso* form of tartaric acid the species $[(VO)_2A_2H_{-2}]^{2-}$ [which probably involves two terdentate tartrate(3−) bridging ligands] was found to be especially stable [see Fig. 4(*b*)] unlike the dimer containing tetradentate tartrate(4−) ligands. This difference in the metal-binding ability of the optically active and the *meso* forms of the ligand was attributed to stereospecific effects because of a nearly eclipsed conformation of the tetradentate *meso*-tartrate in the 2:2 complex.

Also in the case of *meso*-2,3-dimercaptosuccinic acid, the instability of a dimer with a 'cage structure' is certainly responsible for the absence of measurable metal–metal interactions. The kind of EPR spectrum observed suggests, rather than an 'isolated dimer', a polymeric or oligomeric $(VOA)_n$ species either with a linear-chain or a cyclic trimeric structure (see **II** and **III**, respectively). In such cases since the metal ions are at a distance greater than 5–6 Å from each other, dipolar magnetic interactions may cause broadening of the EPR resonances and loss of the hyperfine structure.

Increase of the ligand-to-metal ratio in solution disfavours the formation of the oligomeric $(VOA)_n$ species. For instance, at the H_4dmsucc:VO^{2+} molar ratio of 10:1, EPR spectra show only the presence of magnetically dilute species. In particular over the range pH 4–9 the spectra indicate monomers with $2(CO_2^-, S^-)$ co-ordination, indicated as $[VOA_2H_2]^{4-}$ in Table 3. Owing to the considerable overlap between the complex-formation and ligand-deprotonation processes at lower ligand-to-metal ratios, only the partially deprotonated form of this species, $[VOA_2H]^{5-}$, could be detected by potentiometry. At higher pH a hyperfine constant remarkably lower than those measured for the other mercaptocarboxylate complexes described above is measured. Since in more basic solutions the system does not evolve further, apart from yielding the fully hydrolysed species of VO^{2+} above pH 12, it is likely that this unprecedented species is a bis-chelated complex in which two ligand molecules co-ordinate to the metal ion through (S^-, S^-) couples, resulting in $[VOA_2]^{6-}$ (see Table 4). This is supported by the unique feature of the electronic absorption spectra, in particular the appearance of a single absorption band in the visible region, which can be assigned to a VOS_4 chromophore.

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