Potentiometric and Spectroscopic Studies on Oxovanadium(IV) Complexes of Salicylic Acid and Catechol and Some Derivatives

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The interaction of oxovanadium(IV) with ligands containing phenolate and carboxylate donors, such as salicylic acid, catechol, 2,*x*-dihydroxybenzoic acids (*x* = 3—6), and 3,4-dihydroxybenzoic acid has been studied in aqueous solution by means of potentiometric and spectroscopic (electronic absorption, e.s.r., and electron nuclear double resonance) techniques. Over the low pH range the salicyclic acid-type mode of co-ordination predominates, while the catechol type is preferred in basic media. A mixture of these donor sets is observed in the ternary oxovanadium(IV)–salicylic acid-catechol and binary oxovanadium(IV)-2,3-dihydroxybenzoic acid systems. Besides monomeric complexes, dinuclear species are also formed by the potentially ambidentate dihydroxybenzoic acid derivatives over the intermediate pH range. In the latter complexes both CO_2^- and O^- groups take part in metal bridging.

Recent studies on the interaction of oxovanadium(IV) ions with ligands co-ordinating *via* deprotonated hydroxyl groups[1–3] have shown the strong preference of this ion for such donors. The complex-formation equilibria involved are, however, rather complicated,[1] due to the strong affinity of the hydroxo group itself for binding of oxovanadium(IV) ions, *i.e.* the tendency of oxovanadium(IV) ions to form hydroxo species. The combination of potentiometric and spectroscopic techniques may improve distinctly the reliability of such investigations and the assignment of the species formed.[2,3] Phenolate oxygens have been shown to be very effective donors, especially for copper(II) ions.[4–7] Phenols are also effective ligands for oxovanadium(IV) ions, though the equilibria are not well defined.[8–12] In the cases mentioned above the binding of deprotonated alcoholate or phenolate oxygens to VO^{2+} was the second step in the complex-formation equilibria. Namely, in these complexes a carboxylate group acted as the anchoring site for oxovanadium(IV) ion. In the absence of a binding site readily available at low pH, the hydrolysis of oxovanadium(IV) is favoured over complex formation with a ligand.

The simplest representative of the phenolic ligands provided with an anchoring carboxylate is salicylic acid. Similarly, *o*-diphenolic ligands in which one of the phenolic donors is relatively acidic may be effective in oxovanadium(IV) binding, as indicated earlier.[9–12] Although the oxovanadium(IV)-salicylic acid and -catechol systems have been studied[8,11,12] the equilibrium data seem to be controversial and partly poorly discussed. For instance, e.s.r. and electron nuclear double resonance (ENDOR) spectroscopies, which were shown to be reliable tools for the assignment of the complexes formed,[9,10] clearly indicated that the data presented in ref. 8 are incomplete. In this paper we present a potentiometric and spectral (e.s.r., ENDOR, and electronic absorption) study on the binding ability of various dihydroxybenzoic acids to VO^{2+}. These ligands can be regarded as the derivatives of salicylic acid and/or catechol. Thus, the parent and the mixed-ligand complex formation with the latter ligands has been also studied.

Results and Discussion

The acid–base chemistry of the ligands was studied earlier.[5,7] Here only a list of the acidic groups of each ligand and their p*K* values are given in Table 1 in order to help to explain the metal-binding properties of the ligands. Estimated values for p*K* which could not be determined either pH-metrically or spectrophotometrically are given in parentheses. Accordingly, salicylic acid, catechol, and the 2,*x*-dihydroxybenzoic acids are all regarded as dibasic acids and the fully deprotonated ligand is represented as A^{2-} (with a protonated phenolic hydroxy group in position 2 for the benzoic acids). However, 3,4-dihydroxybenzoic acid is considered as a tribasic acid and its fully deprotonated form is represented as A^{3-}.

The equilibria corresponding to the formation of hydroxo complexes of V^{IV} were taken into account in the calculation of the stability constants of complexes formed in the oxovanadium(IV)–ligand systems. The following species and values taken from the literature[13] were fixed in the evaluation of the pH-metric titration data: $[VO(OH)]^+$ ($\log \beta = -5.66$) and $[\{VO(OH)\}_2]^{2+}$ ($\log \beta = 6.67$).

In the systems of V^{IV} with salicylic acid and its derivatives (2,4-, 2,5-, and 2,6-dihydroxybenzoic acid) precipitation generally occurred at pH 6—7, and pH-metric measurements could be made over the high pH range (up to 8—9) only at high ligand excess. With catechol and its derivatives (2,3- and 3,4-dihydroxybenzoic acid), which can bind V^{IV} more strongly, precipitation due to metal hydrolysis did not occur even at the 1:1 metal-to-ligand molar ratio.

The stability constants of the complexes formed in the vanadium(IV)–ligand systems together with their spectral parameters are listed in Table 2.

Oxovanadium(IV)–Salicylic Acid System.—The potentiometric data indicate the formation of chelate complexes $[VO(A)]$ and $[VOA_2]^{2-}$, as the main species. These complexes are easily seen in the e.s.r. and, especially, in the more unequivocal ENDOR spectra (Table 2, see also ref. 10). The

Table 1. Proton dissociation constants of the ligands at 25 °C and I = 0.2 mol dm^{-3}

Ligand	pK(CO_2H)	pK(OH)[a]	pK(OH)[b]	Ref.
Salicylic acid	2.75	—	13.4	This work
Catechol	—	9.28	13.0	c
Dihydroxybenzoic acid				
2,3-	2.66	9.80	(>14)	5
2,4-	3.11	8.68	(>14)	6
2,5-	2.73	10.05	(>14)	6
2,6-	1.0	13.1	(>14)	6
3,4-	4.25	8.67	12.9	7

[a] pK of the x-OH group in the 2,x-dihydroxybenzoic acid ligands. [b] pK of the second phenolic group. [c] A. Gergely and T. Kiss, *Inorg. Chim. Acta*, 1976, **16**, 51.

Table 2. Stability constants, electronic absorption, e.s.r., and selected ^{1}H ENDOR parameters for oxovanadium(IV) complexes of salicylic acid, catechol, and *o*-diphenolic ligands[a]

			E.s.r.				ENDOR	Absorption
Ligand	Complex	log β	g_0	A_0	$g_{\|\|}$	$A_{\|\|}$	$A_{\|\|}$	$\lambda_{max.}$(ε)
Salicylic acid	[VO(A)]	12.97 ± 0.02	1.967	297	1.956	518	1.70 (H^3), 0.95 (H^6)	790 (25), 575 (6)
	$[VOA_2]^{2-}$	22.81 ± 0.09	1.975	272	1.948[b]	500[b]	1.70 (H^3), 0.95 (H^6)	775 (42), 562 (27)
	$[VOA_2H_{-1}]^{3-}$	13.16 ± 0.05						
	$[VOAH_{-1}]^{-}$	6.32 ± 0.17						
	$[(VOAH_{-1})_2]^{2-}$	16.61 ± 0.08			c			
2,4-Dihydroxy-benzoic acid	[VO(A)]	8.50 ± 0.02	1.967	295	1.942	518	1.70 (H^3), 0.95 (H^6)	795 (26), 575 (8)
	$[VOA_2]^{2-}$	14.22 ± 0.23	1.969	272	1.947[b]	497[b]	1.70 (H^3), 0.95 (H^6)	785 (55), 560 (31)
	$[VOA_2H_{-1}]^{3-}$	5.93 ± 0.21						
	$[VOAH_{-1}]^{-}$	1.48 ± 0.25						
	$[(VOAH_{-1})_2]^{2-}$	8.60 ± 0.17			c			
2,5-Dihydroxy-benzoic acid	[VO(A)]	9.61 ± 0.02	1.967	294	1.944	520	1.70 (H^3), 0.95 (H^6)	793 (28), 572 (8)
	$[VOA_2]^{2-}$	16.43 ± 0.26	1.970	272	1.949[b]	499[b]	1.70 (H^3), 0.95 (H^6)	821 (66), 552 (48)
	$[VOA_2H_{-1}]^{3-}$	7.48 ± 0.12						
	$[VOAH_{-1}]^{-}$	2.49 ± 0.10						
	$[(VOAH_{-1})_2]^{2-}$	10.58 ± 0.09			c			
2,6-Dihydroxy-benzoic acid	[VO(A)]	12.25 ± 0.05	1.970	295	1.942	518	1.70 (H^3)	788 (23), 579 (7)
	$[VOA_2]^{2-}$	21.98 ± 0.22	1.972	272	1.947[b]	497[b]	1.70 (H^3)	800 (45), 565 (28)
	$[VOA_2H_{-1}]^{3-}$	12.04 ± 0.11						
	$[VOAH_{-1}]^{-}$	4.96 ± 0.15						
	$[(VOAH_{-1})_2]^{2-}$	22.92 ± 0.24			c			
Catechol	[VO(A)]	16.75 ± 0.02	1.968	287	1.943	510	1.80 (H^3, H^6)	710 (43), 550 (43)
	$[VOA_2]^{2-}$	31.58 ± 0.03	1.975	246	1.947	462	1.80 (H^3, H^6)	662 (77), 550 (50)
	$[VOAH_{-1}]^{-}$	10.21 ± 0.15						
	$[(VOAH_{-1})_2]^{2-}$	22.92 ± 0.24						
3,4-Dihydroxy-benzoic acid	[VO(AH)]	21.54 ± 0.02	1.970	287	1.939	509	1.80 (H^2, H^5)	685 (66), 565 (71)
	[VOA]$^{-}$	17.13 ± 0.02						
	$[VO(AH)_2]^{2-}$	40.62 ± 0.14						
	$[VOA(AH)]^{3-}$	36.61 ± 0.04	1.975	247	1.954	466	1.80 (H^2, H^5)	650 (85), 550 (60)
	$[VOA_2]^{4-}$	31.42 ± 0.02						
	$[VOAH_{-1}]^{2-}$	11.23 ± 0.10						
	$[(VOAH_{-1})_2]^{4-}$	24.36 ± 0.24						
Catechol–salicylic acid	$[VO(A)B]^{2-}$	27.66 ± 0.04	1.970	262	1.950	482		
2,3-Dihydroxy-benzoic acid	[VO(A)]	9.97 ± 0.04	1.968	296	1.942	517	0.95 (H^6)	796 (28), 563 (9)
	$[VOA_2]^{2-}$	17.25 ± 0.17	1.975	272	1.946	502	0.95 (H^6)	
	$[VOA_2H_{-1}]^{3-}$	10.46 ± 0.15	1.972	258	1.953	481	1.70 (H$^{4'}$), 0.95 (H^6)	661 (46), 532 (238)
	$[VOA_2H_{-2}]^{4-}$	2.00 ± 0.23	1.972	240	1.955	449	1.70 (H^4)	660 (59), 530 (26)
	$[VOAH_{-1}]^{-}$	4.02 ± 0.25						
	$[(VOAH_{-1})_2]^{2-}$	12.86 ± 0.13						
	$[VOAH_{-2}]^{2-}$	−2.88 ± 0.09						
	$[VOAH_{-3}]^{3-}$	−14.13 ± 0.05						

[a] The proton numbering is that usual for the ligands. E.s.r. measurements at ambient temperature and 110 K, ENDOR measurements at 110 K; A values in MHz, λ in nm, and ε in dm^3 mol^{-1} cm^{-1}. The reported ^{1}H ENDOR couplings are the largest splittings, taken from perpendicular spectra, for the aromatic protons adjacent to co-ordinating groups. [b] At 190 K. [c] Intensity decrease in the e.s.r. spectra.

co-ordination of the second ligand molecule is somewhat hindered, $\log(K_{VOA}/K_{VOA_2}) = 3.13$, presumably due to electrostatic reasons. Thus, even at high ligand excess and at pH 6 about 25% of the total amount of oxovanadium(IV) is in the form of monohydroxy mixed-ligand complexes $[VO(A)(OH)]^-$ and $[\{VO(A)(OH)\}_2]^{2-}$ (see Figure 1). The identification of

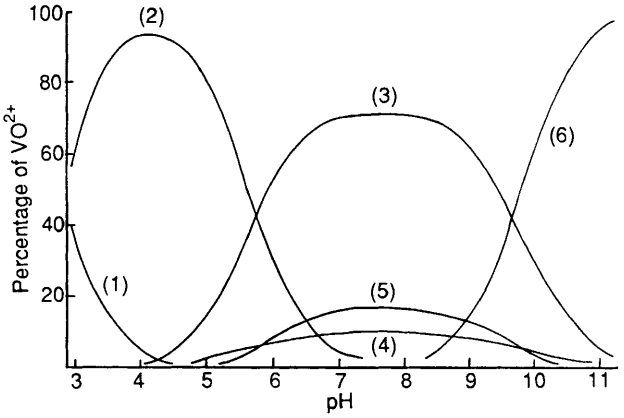


Figure 1. Concentration distribution curves of the complexes formed in the oxovanadium(IV)–salicylic acid system. Concentrations: VO^{2+}, 1×10^{-3}; H_2sal, 8×10^{-3} mol dm^{-3}. Species: (1) VO^{2+}, (2) [VO(A)], (3) $[VOA_2]^{2-}$, (4) $[VOAH_{-1}]^{-}$, (5) $[(VOAH_{-1})_2]^{2-}$, and (6) $[VOA_2H_{-1}]^{3-}$

the $[VO(A)(OH)]^{-}$ species from the spectral data is rather difficult due to its low concentration. The dihydroxo-bridged dimeric form, however, should be e.s.r. silent, and the intensity of these spectra decreases exactly in the same pH range in which the dimeric species is indicated by potentiometric tritrations. The decrease is more distinct at lower ligand excess, since under these conditions the dimer concentration increases considerably. The titration data above pH 7 and at high ligand excess can be fitted well only by assuming the formation of a further species $[VOA_2H_{-1}]^{3-}$, which may be a mixed hydroxo complex. Actually, a significant change of colour from blue to yellow (a shift of $\lambda_{max.}$ from 775 to *ca.* 400 nm) and a continuous weakening of the e.s.r. signals of the $[VOA_2]^{2-}$ species are observed. Thus the process cannot be ascribed to a simple deprotonation of $[VOA_2]^{2-}$, but presumably involves some polymerization which is concomitant with the formation of e.s.r.-silent hydroxo- or oxo-bridged complexes.[14] However, its effect on pH can be taken into account very well by the formation of a single $[VOA_2H_{-1}]^{3-}$ species. Support for the hydrolysis process is provided by the observation that at pH > 12 the final monomeric hydrolytic species $[VO(OH)_3]^{-}$ is detected by e.s.r. and absorption spectroscopy ($g_{\|} = 1.956$, $A_{\|} = 486$ MHz, and $\lambda_{max.} = 420$ nm).

Oxovanadium(IV)–2,x-*Dihydroxybenzoic Acid* (x = 4, 5, *or* 6) *Systems.*—As the pH was not stable enough under strongly basic solutions, likely due to some slow polymer-formation reaction and/or the metal ion-catalysed autoxidation of the ligands, potentiometric data were evaluated only up to pH 8. The species distribution for these systems is similar to that shown in Figure 1. Absorption, e.s.r., and ENDOR spectra indicate very clearly the formation of the [VO(A)] and $[VOA_2]^{2-}$ complexes with a salicylic acid-like co-ordination *via* CO_2^{-},O^{-} donor set(s) (Table 2). The bonding mode is confirmed by the equilibrium constants (log values) calculated for the processes $VO^{2+} + HA^{-} \rightleftharpoons [VO(A)] + H^{+}$ and $[VO(A)] + HA^{-} \rightleftharpoons [VOA_2]^{2-} + H^{+}$ (−0.26 and −2.94, −0.49 and −3.23, and −0.48 and −3.37 for 2,4-, 2,5- and 2,6-dihydroxybenzoic acid, respectively). These constants are in fairly good agreement with those of salicylic acid (−0.43 and −3.59). The formation of the dihydroxo-bridged dimer $[\{VO(A)(OH)\}_2]^{2-}$ could be observed and followed also by the decrease in intensity of the e.s.r. spectrum. In the presence of a ligand excess the deprotonation of $[VOA_2]^{2-}$ takes place. In this process, however, the mixed-hydroxo complex formation (see the salicylic acid system) overlaps with deprotonation of the *x*-phenolic group.

An interesting behaviour of the $[VOA_2]^{2-}$ complexes for all the salicylic acid-type ligands was observed in the e.s.r. spectra. A decrease in temperature caused a splitting of the hyperfine components of the glassy spectra, the coalescence temperature being the same (*ca.* 190 K) with all ligands. This result suggests some dynamic process probably involving the metal–carboxylate bonds.

Oxovanadium(IV)–*Catechol System.*—Two major O^{-},O^{-}-chelated complexes [VO(A)] and $[VOA_2]^{2-}$ are formed at an excess of ligand,[9-12] and are clearly detected by e.s.r. spectroscopy (see Table 2). According to potentiometry, hydroxo complexes (monomeric and dimeric) are also formed at pH 5.0 in equimolar metal–ligand solutions. Since the e.s.r. spectra in this pH range do not show any detectable decrease in intensity, the equilibrium $2[VO(A)(OH)]^{-} \rightleftharpoons [\{VO(A)(OH)\}_2]^{2-}$ seems to be shifted towards the left. Moreover, as substantiated by spectral measurements, the complex $[VOA_2]^{2-}$ and all the bis(catecholate) species formed by the other ligands (see later) are stable to hydrolysis even at pH > 12.

Oxovanadium(IV)–3,4-*Dihydroxybenzoic Acid System.*—In this case the two carboxylate may act as a monodentate donor and the two phenolate oxygens as a binding site of the catecholate type. Potentiometric and spectral data support this prediction, showing that the oxovanadium(IV) ion is bound *via ortho*-phenolate groups in the major species $[VO(A)]^{-}$ and $[VOA_2]^{4-}$ (Table 2). The protonated complexes [VO(AH)], $[VO(AH)_2]^{2-}$, and $[VO(A)(AH)]^{3-}$ also contain O^{-},O^{-}-co-ordinated ligands, but with protonated carboxylic functions. The p*K* values of the carboxylic protons {4.41 for [VO(AH)], 4.01 for $[VO(AH)_2]^{2-}$, and 5.19 for $[VO(A)(AH)]^{3-}$} are somewhat higher than in the free ligand (see Table 1). This is most likely the consequence of a strong electron release from deprotonated phenolic hydroxyl groups.[7] The formation of the major complexes and their protonated forms is supported by the spectral results (Table 2 and refs. 9 and 10). Since there is no distinct decrease in intensity of the e.s.r. spectra at a 1:1 ligand-to-metal molar ratio, as with catechol, the formation of the dihydroxo-bridged dimer $[\{VO(A)(OH)\}_2]$ is negligible with this ligand too. Neither the pH-metric nor the spectroscopic data show any evidence of monodentate carboxylate co-ordination. This is in contrast to the corresponding copper(II) systems, where various monomeric and polymeric complexes were formed through simultaneous co-ordination at both the carboxylate and catecholate binding sites.[7]

Oxovanadium(IV)–*Salicylic Acid* (H_2sal)–*Catechol* (H_2cat) *Ternary System.*—As shown above, both the salicylic acid and catechol types of binding sites are very effective in co-ordination of the oxovanadium(IV) ion. It was then of interest to study the metal-ion competion at the different binding sites and the possibility of mixed co-ordination in the V^{IV}–H_2sal–H_2cat ternary system. Titration data indicate that [VO(sal)] is the major species at the starting pH (4). At higher pH the complexes of H_2cat, which binds V^{IV} more strongly than does H_2sal, predominate. The ternary species $[VO(sal)(cat)]^{2-}$ accounts for about 30% of the total metal ion in equimolar solution. The value of $\Delta\log\beta$ [$\log\beta_{VO(sal)(cat)} - \frac{1}{2}(\log\beta_{VO(sal)_2} + \log\beta_{VO(cat)_2} + \log 4)$] is equal to 0.17, indicating that the formation of the mixed-ligand complex is slightly favoured. The potentiometric results are confirmed by e.s.r. spectra recorded around pH 5 which clearly indicate the formation of [VO(sal)], $[VO(sal)(cat)]^{2-}$, and $[VO(cat)_2]^{2-}$, consistent with the concentration distribution of the species. Since cat is a stronger chelator than sal, in the presence of a ligand excess (1:2:2 metal ion-to-ligand ratio) cat displaces sal from the ternary complex and at higher pH $[VO(cat)_2]^{2-}$ becomes preponderant.

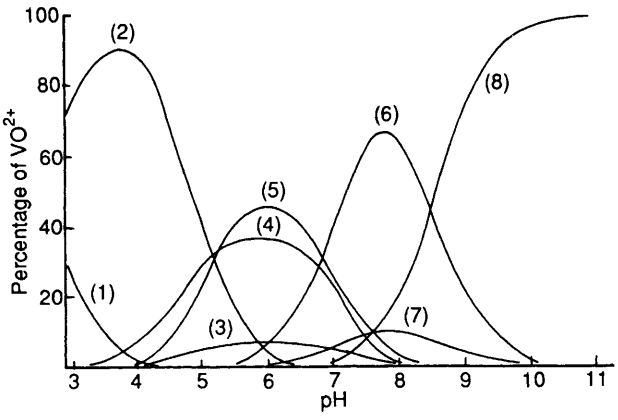
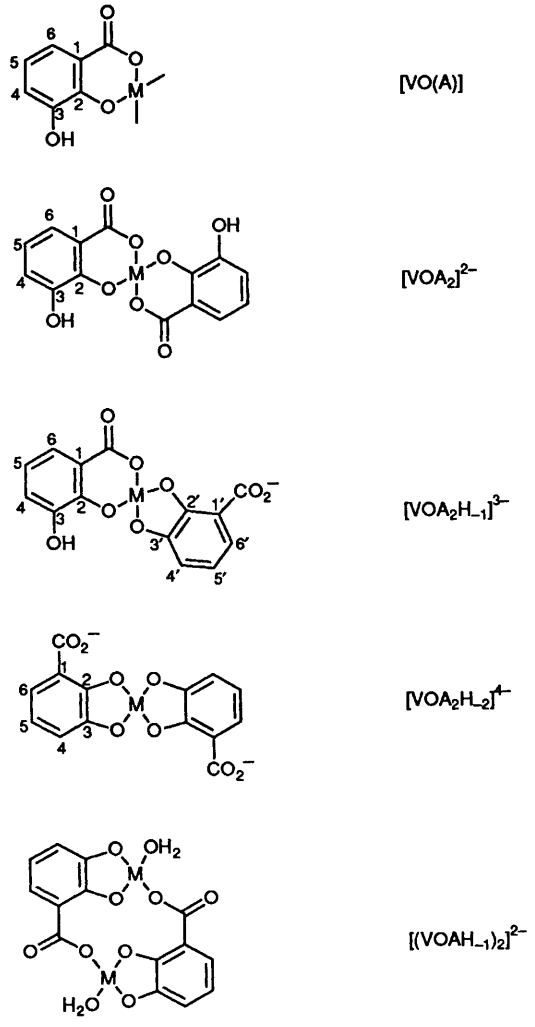


Figure 2. Concentration distribution curves of the complexes formed in the oxovanadium(IV) (2×10^{-3})–2,3-dihydroxybenzoic acid (8×10^{-3} mol dm^{-3}) system. Species: (1) VO^{2+}, (2) [VO(A)], (3) $[VOAH_{-1}]^-$, (4) $[VOA_2]^{2-}$, (5) $[(VOAH_{-1})_2]^{2-}$, (6) $[VOA_2H_{-1}]^{3-}$, (7) $[VOAH_{-2}]^{2-}$, and (8) $[VOA_2H_{-2}]^{4-}$



Scheme. M = VO

Oxovanadium(IV)–2,3-*Dihydroxybenzoic Acid System.*—This acid has three potential binding sites on three adjacent ring carbons and, as such, it could be a good model of the competitive salicylic acid-type (CO_2^-,O^-) and catechol-type (O^-,O^-) chelation in the same molecule. The best set of species which fitted the titration and spectroscopic results is listed in Table 2. A comparison of the stability constants of the species [VO(A)] and $[VOA_2]^{2-}$, relating to the formation reactions $VO^{2+} + HA \rightleftharpoons [VOA] + H^+$ (log $K = -0.13$) and $[VO(A)] + HA^- \rightleftharpoons [VOA_2]^{2-} + H^+$ (log $K = -2.66$), with those of the salicylic acid and 2,*x*-dihydroxybenzoic acid complexes clearly suggests that the salicylic acid type of co-ordination occurs in both species. Examination of the spectral parameters confirms this conclusion. The concentration distribution curves represented in Figure 2 show that over the range pH 4.5—7.5 a dimeric complex $[(VOAH_{-1})_2]^{2-}$ is formed to a high extent even at the excess of ligand. Similarly to the complexes of the other 2,*x*-dihydroxybenzoic acid ligands, this dimer would be a dihydroxo-bridged complex of two salicyclic acid-type VO(A) units. However, the stability data characteristic of the olation reaction $2[VO(A)] \rightleftharpoons [\{VO(A)(OH)\}_2]^{2-} + 2H^+$ reveal that the complex of 2,3-dihydroxybenzoic acid is about two orders of magnitude more stable than those of salicylic acid and its derivatives. Hence, it seems more probable that in this complex two O^-,O^--co-ordinated units are bridged by carboxylate groups (see the Scheme). A similar cyclic dimeric structure was proposed for the corresponding copper(II) complex.[5] An increase in pH leads to hydrolysis of the dimeric form and yields a monomeric hydroxo species $[VOAH_{-2}]^{2-}$ adopting a co-ordination of the catechol type. Some hydroxo-bridged dimer(s) are also formed in this pH range at the 1:1 metal-to-ligand molar ratio as indicated by a decrease in intensity of the e.s.r. spectrum. In the presence of a ligand excess the stepwise deprotonation of the salicylic acid-type $[VOA_2]^{2-}$ takes place to yield $[VOA_2H_{-2}]^{4-}$. According to visible and e.s.r. data (see Table 2 and ref. 9), this process is accompanied by a continuous rearrangement from the salicylic acid to the catechol type of co-ordination *via* the mixed CO_2^-,O^-; O^-,O^- bonding mode. The ENDOR spectra indicate unambiguously the presence of two O^-,O^--co-ordinated ligands in $[VOA_2H_{-2}]^{4-}$.

Conclusion

Ligands containing phenolate and/or carboxylate group(s) can bind V^{IV} strongly and the binding mode depends on the positions of the donors. The salicylate set is a more effective binding site over the acidic pH range, while catecholate acts more efficiently in basic media. Depending on the arrangement of donor groups within the molecule, the simultaneous co-ordination of both binding sites is also possible. Various monomeric and dimeric species exhibiting mixed bonding modes CO_2^-,O^-; O^-,O^- or tridentate (CO_2^-,O^-,O^-) co-ordination are formed by 2,3-dihydroxybenzoic acid in which the donor groups are placed on adjacent ring carbon atoms. The strong hydrolysis tendency of the VO^{2+} ion, even when metal-bound, complicates the equilibria existing in basic media and further studies are needed for their full understanding. It should be also noted that the *o*-catecholic ligands, being able to displace the oxo group from the VO^{2+} ion, may form complexes of the tris(catecholato)vanadate(IV) type.[15,16] However, the extent of such a reaction, which is favoured in concentrated solutions by high ligand-to-metal molar ratios, is negligible under the conditions used in this work. A detailed study is in progress to evaluate the stability of these complexed species.

Experimental

Potentiometric Measurements.—Stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated by the PSEQUAD program,[17] using pH-metric titration data. The ligand concentration in the samples (25 cm^3) was 0.004 or 0.002 mol dm^{-3} and the metal-to-ligand ratios were 0:1, 1:1, 1:2, 1:4, 1:6,

and 1:8. The ionic strength was 0.2 mol dm^{-3} (KCl). The titrations were performed at 25 °C over the range pH 2.5—11.0 or, depending on the molar ratio, until precipitation occurred. The pH was measured by a Radiometer pHM84-meter using G2040B glass and K4040 calomel electrodes. Since most of the ligands tended to undergo oxidation, all measurements were performed in a TTA 80 titration unit under an argon atmosphere. The electrode was calibrated by the method of Irving *et al.*[18] so that the pH-meter readings could be converted into hydrogen-ion concentrations.

Spectroscopic Measurements.—Electronic absorption spectra were recorded on a Beckman Acta MIV spectrophotometer, e.s.r. and ^1H ENDOR spectra with a Bruker 220 D instrument operating at the *X*-band frequency (≈9.40 GHz) and equipped with a Bruker ENDOR accessory. Instrumental settings: microwave power, 50 mW; radiofrequency power at 14 MHz, 100 W; frequency modulation depth, 10–100 kHz. ENDOR spectra were recorded, at *ca.* 110 K, by setting the magnetic field on the parallel, $M_I = -\frac{5}{2}$, or perpendicular, $M_I = -\frac{3}{2}$, e.s.r. resonances.

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