Copper(II) and Oxovanadium(IV) Complexes of 2,3-Dihydroxyterephthalic and 2,3,4-Trihydroxybenzoic Acids

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The complexes formed by 2,3-dihydroxyterephthalic and 2,3,4-trihydroxybenzoic acids with copper(II) and oxovanadium(IV) in aqueous solution were studied by spectroscopic and potentiometric techniques. The results show that all of the functional groups of the ligands are involved in complex formation. Rather stable di- and tri- or tetra-meric species were detected with both metal ions. While the former are EPR-silent, the latter could be characterised by EPR spectroscopy.

In living systems, like plants or microorganisms, simple aromatic compounds bearing phenolic and carboxylic groups serve as versatile ligands to chelate toxic and nutrient metal ions. Most of these compounds are also found in the natural environment as by-products of metabolic and degradation processes and they act as non-specific ligands toward metal ions in terrestrial and aquatic systems. For instance, it was observed that catecholic compounds are responsible for the complexation of exogenous oxovanadium(IV) ions in plant roots, probably being produced and released in response to the stress induced by a high metal concentration in the external medium.[1]

With this class of ligands, very efficient chelating ability is achieved through several potential donor sets *e.g.* of salicylic and *o*-catecholic type.[2-6] Also mixed salicylic-*o*-catecholic co-ordination can yield rather stable complexed species. In natural conditions, the very strong catecholic type of co-ordination can lead also to unusual complexes like the tris(catecholato) species containing bare V^{IV}, *e.g.* with tannic compounds.[7] These complexes may have relevant implications for natural systems since non-oxo vanadium complexes are often involved in the storage and accumulation of vanadium in natural systems. Polynuclear species may also be formed with ligands exhibiting ambidentate behaviour, *e.g.* those able to bind a metal ion through a donor set while retaining further donors to co-ordinate another metal ion. These processes may be significant due to their involvement in the natural processes leading to the formation of humic and fulvic compounds, heterogeneous polyfunctional macromolecules, which, being the final products of chemical and biological decomposition processes, are present everywhere in the environment as major components of both dissolved and particulate organic matter. Actually, although very complicated in principle, the structure of these humic substances consists of a limited number of building blocks, most of them being hydroxycarboxylic aromatic residues.

In continuation of our previous studies on the co-ordination modes of 2,*x*-dihydroxybenzoic acids ($x = 3$–6), which exhibit prevalently the salicylate type of co-ordination,[2,3,6] as well as of 3,4-dihydroxybenzoic acid and its analogues,[4-6] which can be considered as effective diphenolate donors, we have extended our studies to the complexes of 2,3-dihydroxyterephthalic (2,3-dhtpa) and 2,3,4-trihydroxybenzoic (2,3,4-thba) acids. These ligands have four adjacent carboxylic and phenolic donor functions on the aromatic ring which make them potentially interesting chelators of Cu^{II} and $V^{IV}O$. The complexes formed by these metal ions have been studied in detail by use of spectroscopic and potentiometric techniques. The results reported here demonstrate further that, even in solution, the polyfunctional and ambidentate nature of these compounds leads to oligomeric species and proves that complexation to metal ions provides natural organic matter with cross-linking points favouring aggregation and polymerisation processes.

Experimental

Chemicals.—2,3,4-Trihydroxybenzoic acid (97% purity) was an Aldrich product, whereas 2,3-dihydroxyterephthalic acid was synthesised by the method given in ref. 8. The purity of the ligands was checked and the exact concentration of their solutions was determined by the Gran method.[9] A VO^{2+} stock solution, prepared as described in ref. 10, was standardised for metal concentration by permanganate titration and for hydrogen ion concentration by potentiometry using the appropriate Gran function. The concentration of the Cu^{2+} stock solution was measured gravimetrically *via* precipitation of the quinolin-8-olate. The ionic strength of the samples was adjusted to 0.2 mol dm^{-3} KCl. In all cases the temperature was 25.0 ± 0.1 °C.

Potentiometric Studies.—The stability constants of the proton and metal complexes of the ligands were determined by pH-metric titration of 25 cm^3 samples. The concentration of the ligands was (2 or 4) $\times 10^{-3}$ mol dm^{-3} for 2,3,4-thba and 8×10^{-4} mol dm^{-3} for 2,3-dhtpa due to the poorer solubility of the latter ligand. The molar ratio between the metal ion and ligand was 1 : 1, 1 : 2, 1 : 3 or 1 : 4. Titrations were performed over the pH range 2–11, or until precipitation occurred, with a KOH solution of known concentration (*ca.* 2×10^{-1} mol dm^{-3}) under a purified argon atmosphere in order to avoid the oxidation of the ligands or VO^{2+} ion. The reproducibility of the titration curves was within 0.005 pH units over the whole pH range. The equilibria corresponding to the formation of hydroxo complexes of VO^{2+} were taken into account in the calculation of the stability constants. The following species were assumed: $[VO(OH)]^+$ ($\log \beta_{1-1} = -5.94$), $[\{VO(OH)\}_2]^{2+}$ ($\log \beta_{2-2} = -6.95$), and $[VO(OH)_3]^-$ ($\log \beta_{1-3} = -18.0$), calculated from literature data[11] using the Davis equation to take into account the different ionic strength.

The pH was measured with a Radiometer pHM 84 instrument and a G2040B combined electrode, calibrated for hydrogen ion concentration according to Irving *et al.*[12] A pK_w value of 13.76 was determined and used for the titrations at 25 °C and $I = 0.2$ mol dm^{-3} KCl. The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated by the PSEQUAD computer program.[13]

Spectroscopic Studies.—In order to establish the metal ion binding sites in the metal complexes, electronic absorption and EPR studies were carried out. Absorption spectra were recorded in the visible and UV wavelength range with a Beckman Acta MIV spectrophotometer. In the case of the 2,3,4-thba system accurate spectra could not be obtained in the visible range as the high-intensity ligand bands and ligand-to-metal charge-transfer bands fully covered the d–d absorptions. Isotropic and anisotropic X-band EPR spectra (9.15 GHz) were recorded at 298 or 140 K using a Varian E-9 spectrometer. As is usual, the samples for low-temperature measurements were added with a few drops of dimethyl sulfoxide to ensure good glass formation in frozen solutions. The composition of the samples and experimental conditions were the same as described for the potentiometric titrations.

Results and Discussion

Proton Complexes of 2,3-*Dihydroxyterephthalic and* 2,3,4-*Trihydroxybenzoic Acids.*—Both ligands contain four acidic protons in adjacent positions on the aromatic ring. However, in each ligand, only two of them dissociate in the measurable pH range (up to pH 13.5), namely two carboxylic groups in the case of 2,3-dhtpa and one carboxylic and one phenolic group in the case of 2,3,4-thba (see Table 1). The very weak acidity of the remaining two protons in each molecule may be attributed to the electrostatic attraction of the nearby negative charges as well as to hydrogen-bond formation between the carboxylate or the phenolate and the undissociated phenolic hydroxyl functions. Similar results were found for the parent molecules, salicylic acid and catechol, and also for other aromatic hydroxycarboxylates.[2,3]

Copper(II) *and Oxovanadium*(IV) *Complexes of* 2,3-dhtpa.—An analysis of the titration curves measured at different metal ion-to-ligand molar ratios revealed a distinct difference in the metal binding ability of the ligand towards copper(II) or oxovanadium(IV). Namely, as Fig. 1 shows, oxovanadium(IV) co-ordinates to the ligand somewhat more strongly than copper(II) and, more importantly, a significant pH-jump can be observed at different base consumptions. This sudden pH change is independent of the extent of ligand excess. However, the jump from pH 5 to 9 occurs at an extra base consumption of $1.5c_{Cu}$ in the copper(II)–2,3-dhtpa system and of $2.0c_{VO}$ with oxovanadium(IV). This may suggest the formation of a single species in this pH range with a stoichiometry of $(CuA_xH_{-1.5})_n$ or $(VOA_xH_{-2})_n$, respectively. The EPR spectral data listed in Table 2 indicate mono- and bis-complexes with carboxylate co-ordination to copper(II) in the range pH 2–4, besides a significant amount of free Cu^{2+} ion, chelation of the salicylate at pH 4–5 and copper(II) in two different chemical environments, presumably with CO_2^-, O^- and $2(CO_2^-, O^-)$ bonding modes at pH 7–9. At higher pH the spectrum becomes more complex resembling a mixture of magnetically dilute and coupled copper(II) complexes (see later).

At the same time, the isotropic spectra of the oxovanadium(IV)–2,3-dhtpa system, while indicating at first the formation of monodentate carboxylate co-ordinated complexes, *e.g.* through a small decrease of the isotropic ^{51}V coupling constant as compared to that of the free aqua-ion, and then a 1 : 1 salicylate chelated species until pH 5, display a 22-line pattern in the range pH 5–11 (see Fig. 2), resembling closely those of the cyclic trimer found in the $V^{IV}O$–pyrophosphate system.[14,15] The ^{51}V hyperfine coupling constant is nearly one-third of that expected for a monomeric species with the same donor set around the metal ion. Low-temperature frozen-solution spectra also exhibit a resolved hyperfine structure, superimposed on a broad resonance at *g* about 1.949, consisting of 22 lines with a coupling

Table 1 Protonation constants of the ligands (H_2A) at $I = 0.2$ mol dm^{-3} and 25 °C*

Ligand	log $K(HA^-)$	log $K(H_2A)$
2,3-dhtpa	2.89(1)	1.93(5)
2,3,4-thba	8.65(1)	3.07(2)

* $K(HA) = [HA^-]/[H^+][A^{2-}]$ dm^3 mol^{-1}, $K(H_2A) = [H_2A]/[HA^-][H^+]$ dm^3 mol^{-1}.

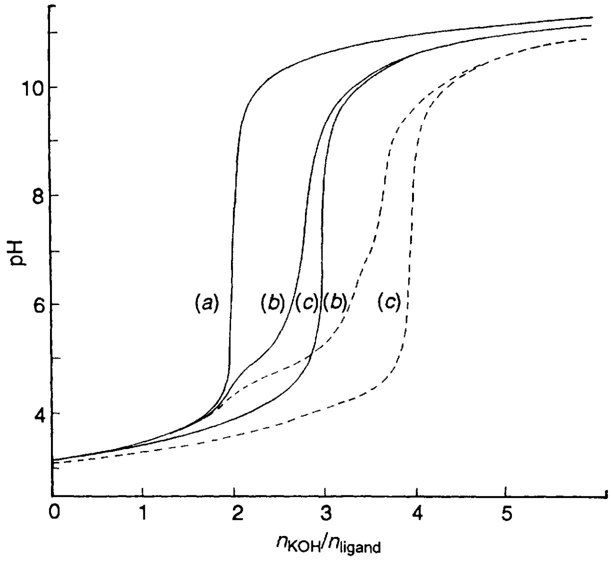


Fig. 1 Titration curves for the (*a*) H^+-, (*b*) Cu^{II}- and (*c*) $V^{IV}O$-2,3-dhtpa systems at 1 : 2 (——) and 1 : 1 (– – – –) metal ion-to-ligand molar ratios

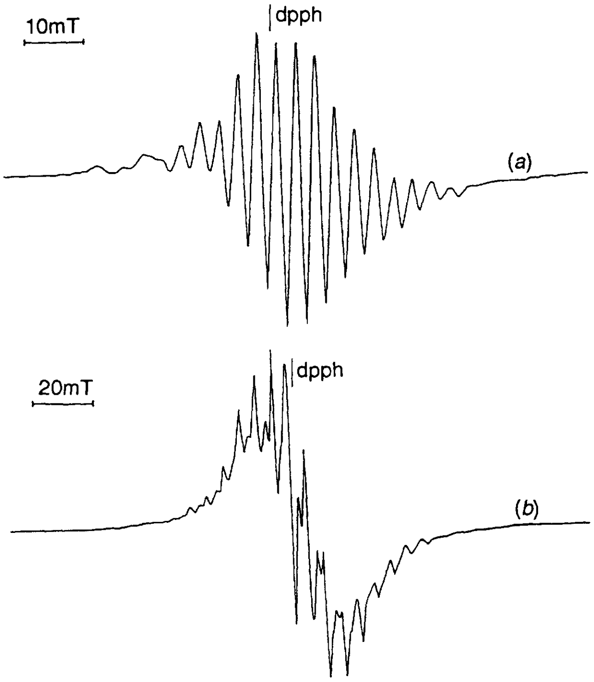


Fig. 2 EPR spectra of the cyclic trimer formed in the $V^{IV}O$–2,3-dhtpa system at pH 6.8 recorded (*a*) at room temperature and (*b*) at 110 K (dpph = diphenylpicrylhydrazyl)

Table 2 EPR spectral data for the complexes

Ligand	Ion	$g_{\parallel}$	$A_{\parallel}/10^{-4}$ cm^{-1}	g_0	$A_0/10^{-4}$ cm^{-1}	Donor set	Species
2,3-dhtpa	Cu^{II}	2.380	133			CO_2^-	[CuA]
		2.351	154			$2(CO_2^-)$	
		2.327	158			CO_2^-, O^-	$[CuAH_{-1}]^-, [Cu_2A_2H_{-3}]^{3-}, [Cu_3A_3H_{-5}]^{5-}$
		2.288	176			$2(CO_2^-, O^-)$	$[Cu_2A_2H_{-3}]^{3-}, [Cu_3A_3H_{-5}]^{5-}$
		2.265	195			$CO_2^-, O^-; O^-, O^-$	$[CuA_2H_{-3}]^{5-}$
		2.310	62			$2(CO_2^-, O^-)$	$[Cu_3A_3H_{-6}]^{6-}$
	V^{IV}O	1.943	172	1.967	98	CO_2^-, O^-	$[VOAH_{-1}]^-, [(VO)_2A_2H_{-3}]^{3-}$
		1.950	164	1.969	90	$2(CO_2^-, O^-)$	$[(VO)_2A_2H_{-3}]^{3-}$
		1.954	159	1.968	85	$CO_2^-, O^-; O^-, O^-$	$[VOA_2H_{-3}]^{5-}$
		1.949	54	1.983	30	$2(CO_2^-, O^-)$	$[(VO)_3A_3H_{-6}]^{6-}$
2,3,4-thba	Cu^{II}	2.239	201			$2(O^-, O^-)$	$[CuA_2H_{-2}]^{4-}$
	V^{IV}O	1.943	172	1.967	99	CO_2^-, O^-	[VOA]
		1.952	161	1.968	86	$CO_2^-, O^-; O^-, O^-$	$[VOA_2H_{-1}]^{3-}$
		1.954	155	1.973	82	$2(O^-, O^-)$	$[VOA_2H_{-2}]^{4-}$
		1.965	39	1.971	22	$CO_2^-, O^-; O^-, O^-$	$[(VO)_4A_4H_{-8}]^{8-}$

Table 3 Stability constants (log β) of the copper(II) and oxovanadium(IV) complexes of 2,3-dhtpa at $I = 0.2$ mol dm^{-3} (KCl) and 25 °C

Species	Copper(II)	Oxovanadium(IV)
[MA]	2.0(2)	3.2(2)
$[MAH_{-1}]^-$	−1.90(5)	0.31(4)
$[M_2A_2H_{-3}]^{3-}$	−4.43(6)	−0.5(4)
$[M_3A_3H_{-5}]^{5-}$	−9.50(5)	—
$[M_3A_3H_{-6}]^{6-}$	−18.13(9)	−4.39(9)
$[MA_2H_{-3}]^{5-}$	−16.15(9)	−10.86(9)
Fitting*	5.92×10^{-3}	4.60×10^{-3}
No. of points	215	197

* The average difference between the experimental and calculated titration curves expressed in cm^3 of the titrant.

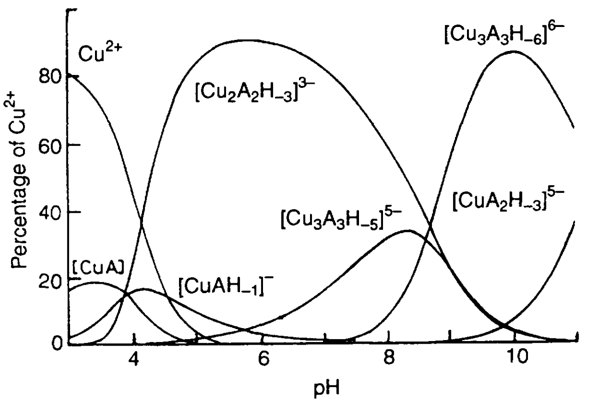


Fig. 3 Concentration distribution curves for the complexes formed in the copper(II)–2,3-dhtpa system, $c_{Cu} = 2 \times 10^{-3}$, $c_{ligand} = 4 \times 10^{-3}$ mol dm^{-3}

constant of *ca.* 54 × 10^{-4} cm^{-1}. This value corresponds closely to that expected for the parallel coupling of a trimeric species [55 × 10^{-4} cm^{-1} based on the parameters measured for the parent oxobis(salicylato)vanadium(IV) complex].[6] In the presence of an excess of ligand (2,3-dhtpa : V^{IV}O ⩾ 2 : 1) the EPR spectra of these systems indicate the presence of monomeric complexes with CO_2^-, O^-; O^-, O^- mixed bonding mode at pH > 11.5. It is noteworthy that purely O^-, O^--co-ordinated complexes could not be detected in either of these systems until pH 12. The formation of an EPR-active copper(II) trimer is indicated also in the copper(II)–2,3-dhtpa system at pH > 9 by spectra recorded in frozen solution. In such a case, ten hyperfine lines with intensity ratios 1:3:6:10:12:12:10:6:3:1 are expected, but only eight of them are clearly distinguishable in the experimental spectrum. However, the value of the coupling constant is again about one third of that expected for a monomeric bis(salicylate) co-ordinated copper(II) species. Electronic absorption spectral parameters of the complexes support these findings. Namely, the continuous shift of the d–d absorption band from 750 nm (ε = 104 dm^3 mol^{-1} cm^{-1}) to 625 nm (ε = 116) while the pH is increased from 5 to 9 is in accordance with a change in the bonding mode from CO_2^-, O^- to $2(CO_2^-, O^-)$. The somewhat higher intensity of these bands, especially at lower pH, as compared with those of the salicylic acid derivatives 2,*x*-dhba [CO_2^-, O^- 720–740 nm (ε = 40–60 dm^3 mol^{-1} cm^{-1}); $2(CO_2^-, O^-)$ 620–650 nm (ε = 100–140 dm^3 mol^{-1} cm^{-1})],[2] may be attributed to the occurrence of these bonding modes in a chain-like oligomeric structure. In the pH range 10–11 the spectra do not change and are practically independent of the metal ion-to-ligand ratio; they show unique spectral parameters, 605 nm (ε = 110 dm^3 mol^{-1} cm^{-1}) and 440 (sh, 680), different from those obtained for other copper(II) complexes of salicylic acid derivatives.[2] These spectral parameters probably can be ascribed to the cyclic trimeric complex.

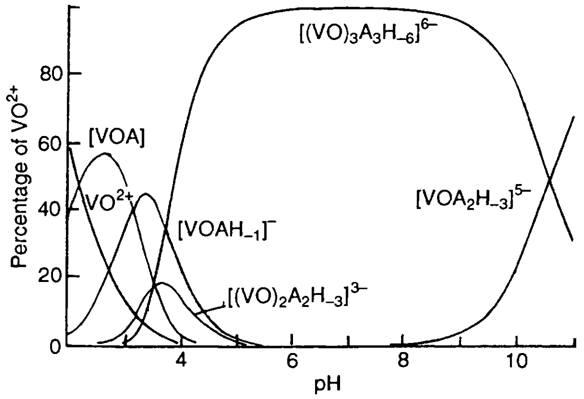
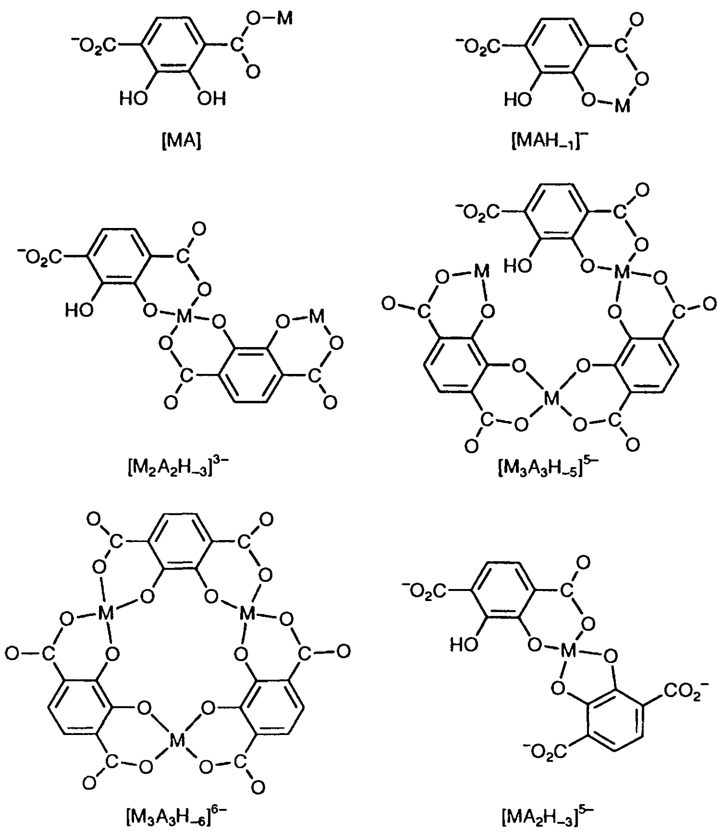


Fig. 4 Concentration distribution curves for the complexes formed in the oxovanadium(IV)–2,3-dhtpa system, $c_{VO} = 2 \times 10^{-3}$, $c_{ligand} = 4 \times 10^{-3}$ mol dm^{-3}

Similarly, the visible spectra display practically no change in the formation pH range of the cyclic trimeric species in the V^{IV}O–2,3-dhtpa system [750 nm (ε = 48 dm^3 mol^{-1} cm^{-1}), 545 (40) and 405 (980)]. In the case of ligand excess and pH > 10, however, the spectra show an extra band around 700 nm in a strong overlap with the absorption band of the trimer at 750 nm. This extra band can be ascribed[6] to the monomeric bis(complex) with CO_2^-, O^-; O^-, O^- mixed bonding mode. The pure $2(O^-, O^-)$ co-ordination would result in absorption bands at higher wavelengths around 650 and 530 nm.[2,6] In



Scheme 1

Table 4 Derived equilibrium constants for the formation of salicylate-type complexes

Ligand *	Process	Cu^{II}	$V^{IV}O$
H_2sal	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.80	−0.43
2,4-dhba	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.91	−0.18
2,5-dhba	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.87	−0.44
2,6-dhba	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.91	−0.85
2,3-dhba	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.24	+0.17
2,3-dhtpa	$M^{2+} + A^{2-} \rightleftharpoons [MAH_{-1}] + H^+$	−1.90	+0.31
2,3,4-thba	$M^{2+} + HA^- \rightleftharpoons [MA] + H^+$	−2.91	−0.10

* H_2sal = Salicylic acid, dhba = dihydroxybenzoic acid.

acidic solution the mono(salicylato) complex was identified by the absorptions at 790 and ≈550 nm,[6] the latter being strongly merged into the ligand-to-metal charge transfer band near 400 nm.

Taking into account the above mentioned potentiometric, electronic absorption and EPR behaviour of these systems, the pH-metric titration curves were evaluated by the assumption of various CO_2^-- and CO_2^-, O^--co-ordinated monomeric and oligomeric (chain and cyclic di- and tri-meric) species. The best fit was obtained by the assumption of the species given in Table 3. Other monomeric species, like $[M(HA)]^+$, $[MA_2]^{2-}$, $[MA_2H_{-1}]^{3-}$, $[MA_2H_{-2}]^{4-}$ and oligomeric species, like M_2AH_{-2} (with co-ordination at both salicylate ends of the molecule), were rejected by the computer program during calculation. The concentration distribution curves for the two systems are depicted in Figs. 3 and 4, while the suggested bonding modes of the complexes are shown in Scheme 1.

For a comparison, proton displacement stability constants of the 1 : 1 copper(II) and oxovanadium(IV) complexes of salicylic acid and various derivatives of salicylic acid are listed in Table 4.[2,3,5] These data clearly show that the presence of a phenolic OH group in adjacent position to the co-ordinating phenolate will increase, by about a 0.5–1 order of magnitude, the stability of the salicylate co-ordinated copper(II) or oxovanadium(IV) complexes, as compared to the corresponding complexes of the parent ligand, salicylic acid itself. On the other hand, phenolic OH groups in other positions on the aromatic ring will practically not affect the metal binding ability of the salicylate site.

Copper(II) *and Oxovanadium*(IV) *Complexes of* 2,3,4-thba.—The copper(II) binding ability of 2,3,4-thba resembles very much that of 2,3-dhba (2,3-dhba = 2,3-dihydroxybenzoic acid) which contains only two phenolic OH protons in the aromatic ring. This latter ligand was shown to form salicylate-type complexes at acidic pH and catecholate-type complexes at pH > 10.[3] In spite of the preference of copper(II) for O^-, O^- co-ordination, over the acidic pH range, where the proton is an effective competitor at this binding site, the less basic salicylate site co-ordinates the metal ion. In the intermediate pH range, the formation of various chain-like di- and tri-meric species and a cyclic dimer with composition $Cu_2A_2H_{-2}$ as a major species was proposed. In this cyclic dimer the carboxylate groups link two O^-, O^--co-ordinated units together. The ligand 2,3,4-thba seems to follow the same complexation pattern as 2,3-dhba. By pH≈6.5, beside the carboxylic H^+, two extra protons are liberated from the ligand due to metal ion co-ordination (see Fig. 5), which corresponds to a species with composition $(CuAH_{-1})_n$. This species, which dominates in the pH range 5–7, is likely to be a dimer. However, it cannot be a magnetically dilute dimer, as in the case of 2,3-dhba, because no EPR-active species could be detected in this pH range. Hence, we assume that the most probable structure of this complex is a *O*-phenolate-bridged dimer (see Scheme 2), in which the antiferromagnetically coupled copper(II) centres yield an EPR-inactive complex. The formation of similar species was suggested in the copper(II)–[amino(2′,3′-dihydroxyphenyl)-methyl]phosphonic acid (the phosphono derivative of 2,3-dihydroxyphenylglycine) system.[16]

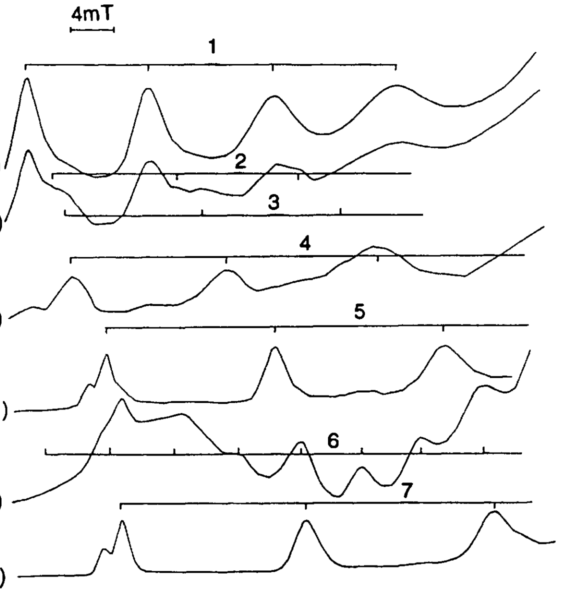
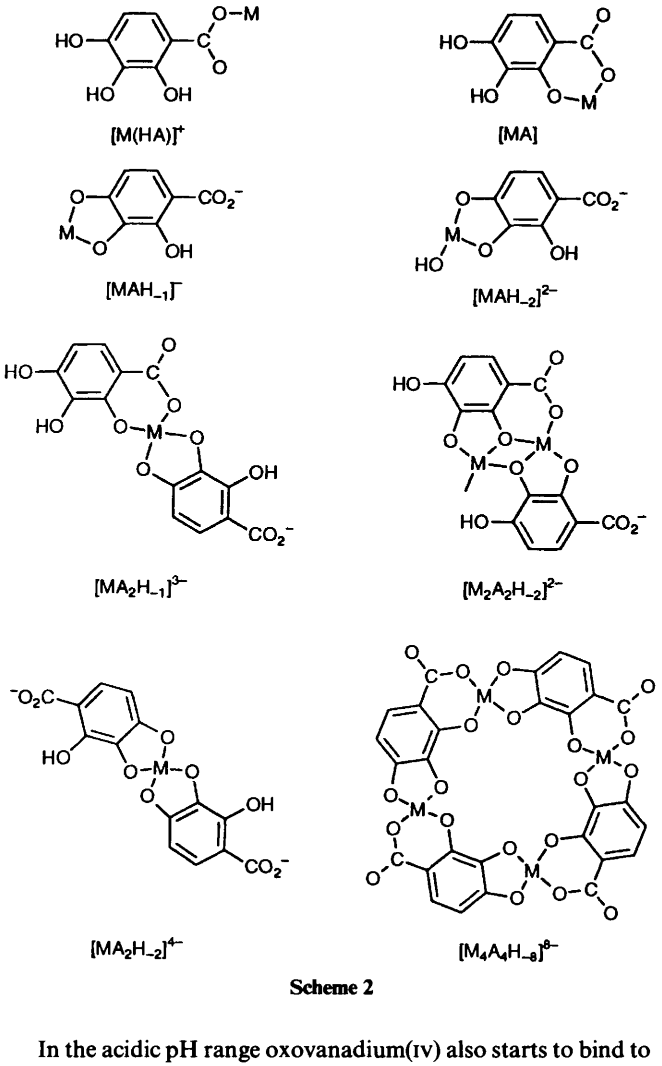


Fig. 5 Parallel region of the frozen-solution EPR spectra of the Cu^{II}–2,3-dhpta system at 1:2 metal ion-to-ligand molar ratio and varying pH: (*a*) pH 3.3, (*b*) 3.9, (*c*) 5.3, (*d*) 7.0, (*e*) 10.0, (*f*) 12.0. The copper hyperfine structure for the aqua-ion (1) and the donor sets CO_2^- (2), $2CO_2^-$ (3), CO_2^-, O^- (4), $2(CO_2^-, O^-)$ (5), $2(CO_2^-, O^-)$ in the trimer $[Cu_3A_3H_{-6}]^{6-}$ (6) and CO_2^-, O^-; O^-, O^- (7) is indicated



Scheme 2

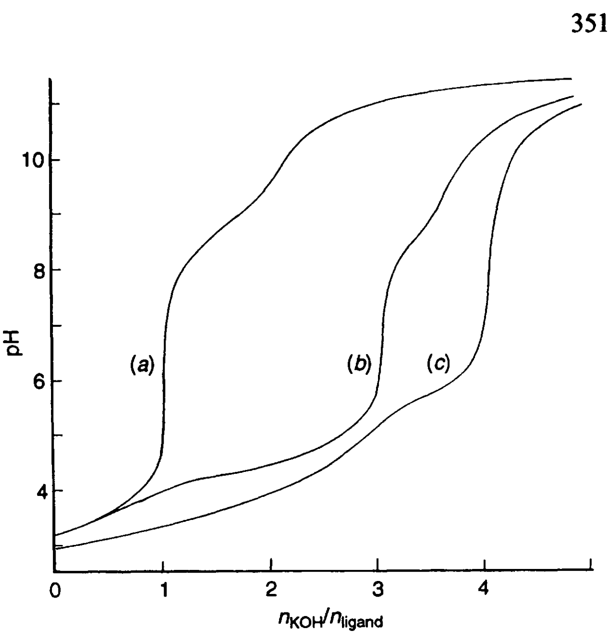


Fig. 6 Titration curves for the (*a*) H^+–, (*b*) Cu^{II}– and (*c*) $V^{IV}O$–2,3,4-thba systems at 1:1 metal ion-to-ligand molar ratio

In the acidic pH range oxovanadium(IV) also starts to bind to 2,3,4-thba at the carboxylate group and then at the salicylate site forming complexes of composition $[VO(HA)]^+$ and [VOA], respectively. Due to the higher affinity of the metal ion toward the catecholate binding site, there is a rearrangement of the bonding mode to O^-, O^- co-ordination with a pK ≈4.3. EPR spectra indicate unambiguously oxovanadium(IV) in mono- and bis-salicylate (minor) co-ordination as the pH is raised from 2 to 5. In the case of an excess of ligand, monomeric complexes are formed with the CO_2^-, O^-; O^-, O^- mixed bonding mode $\{[VOA_2H_{-1}]^{3-}\}$ at around neutral pH, and with pure catecholate O^-, O^-; O^-, O^- co-ordination $\{[VOA_2H_{-2}]^{4-}\}$ at alkaline pH. At 1:1 (or lower) metal ion-to-ligand molar ratio, the EPR spectra are rather complex and, at pH >6, indicate an equilibrium between an O^-, O^--co-ordinated monomeric species and a polynuclear species. This polynuclear species is detected well at 1:2 metal-to-ligand molar ratio and pH *ca.* 7 (see Fig. 5). It can be observed that there is also a slight shift towards monomer formation as the pH is raised from ≈6 (where according to the pH-metric titration curve a significant jump to pH 10 occurs, see Fig. 6) to pH≈11. The number of protons liberated during the pH jump is 3.0, *i.e.* the ligand is bound in the complex in fully deprotonated form $H_{-2}A$ (the other two very weakly acidic phenolic OH groups are also deprotonated). This can occur most likely in cyclic oligomeric complexes with composition $(VOAH_{-2})_n$ where all four donor atoms of the ligands are co-ordinated to the metal ions, although other possibilities such as open-chain polymeric species or deprotonation under the influence of the nearby positive charge without direct co-ordination cannot be completely excluded. The oligomeric species formed by $V^{IV}O$ with the 2,3,4-thba ligand does not exhibit complete resolution in the isotropic EPR spectra recorded at room temperature. However, the measured value of the hyperfine coupling constant (22×10^{-4} cm^{-1}) is consistent with a tetrameric arrangement of four equivalent metal ions. Actually, this value is exactly that predicted by comparison with the monomeric complex formed by *o*-catechol and salicylic acid exhibiting a O^-, O^-; CO_2^-, O^- binding mode.[6] Moreover the frozen-solution spectra show almost all of the 29 ^{51}V parallel resonances expected in the case of four coupled oxovanadium(IV) ions in equivalent environments. In this case too, the value of the coupling constant is about one fourth of that expected for the corresponding monomer with mixed salicylate–catecholate co-ordination at the metal ion.[6] As suggested by the EPR spectra, a monomer $\rightleftharpoons$ tetramer equilibrium occurs, the monomeric species exhibiting $VOAH_{-2}$ stoichiometry being

Table 5 Stability contants (log β) of the copper(II) and oxovanadium(IV) complexes of 2,3,4-thba at I = 0.2 mol dm^{-3} (KCl) and 25 °C

Species	Copper(II)	Oxovanadium(VI)
$[M(HA)]^+$	10.60(6)	11.36(9)
$[MA]$	6.91(5)	8.72(3)
$[MAH_{-1}]^-$	—	4.49(2)
$[M_2A_2H_{-2}]^{2-}$	8.50(4)	—
$[MAH_{-2}]^{2-}$	—	−1.41(10)
$[M_4A_4H_{-8}]^{8-}$	—	4.89(9)
$[MA_2H_{-1}]^{3-}$	6.03(5)	10.24(9)
$[MA_2H_{-2}]^{4-}$	−2.27(3)	4.88(6)
Fitting*	5.38 × 10^{-3}	7.65 × 10^{-3}
No. of points	184	168

* The average difference between the experimental and calculated titration curves expressed in cm^3 of the titrant.

Table 6 Derived equilibrium constants for the formation of catecholate-type complexes

Ligand*	Process	Cu^{II}	V^{IV}O
H_2cat	$M^{2+} + H_2A \rightleftharpoons [MA] + 2H^+$	−8.46	−5.02
	$M^{2+} + 2H_2A \rightleftharpoons [MA_2]^{2-} + 4H^+$	−19.87	−12.98
3,4-dhba	$M^{2+} + H_2A^- \rightleftharpoons [MA]^- + 2H^+$	−7.82	−5.44
	$M^{2+} + 2H_2A^- \rightleftharpoons [MA_2]^{4-} + 4H^+$	−18.52	−12.12
2,3-dhba	$M^{2+} + HA^- \rightleftharpoons [MAH_{-1}]^- + 2H^+$	—	−5.72
	$M^{2+} + 2HA^- \rightleftharpoons [MA_2H_{-2}]^{4-} + 4H^+$	−24.40	−17.60
2,3,4-thba	$M^{2+} + HA^- \rightleftharpoons [MAH_{-1}]^- + 2H^+$	—	−4.16
	$M^{2+} + 2HA^- \rightleftharpoons [MA_2H_{-2}]^{4-} + 4H^+$	−19.57	−12.38

* H_2cat = Catechol.

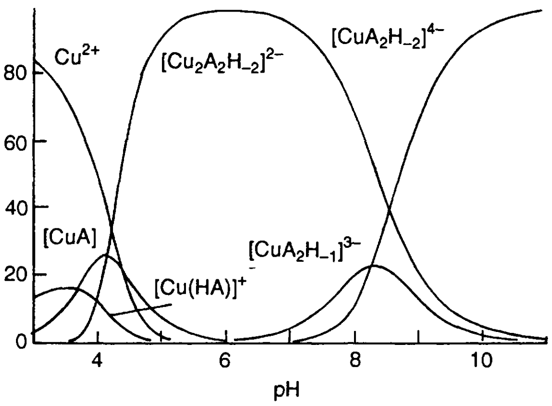


Fig. 7 Concentration distribution curves for the complexes formed in the copper(II)–2,3,4-thba system, c_{Cu} = 2 × 10^{-3}, c_{ligand} = 4 × 10^{-3} mol dm^{-3}

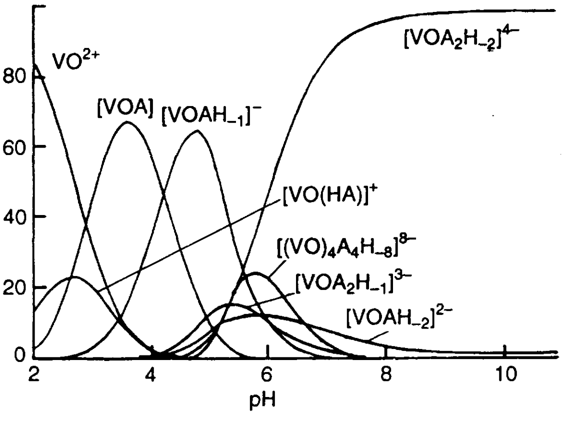


Fig. 8 Concentration distribution curves for the complexes formed in the oxovanadium(IV)–2,3,4-thba system, c_{VO} = 2 × 10^{-3}, c_{ligand} = 4 × 10^{-3} mol dm^{-3}

attributable with a O^-, O^--co-ordinated mixed hydroxo species $[VOAH_{-1}(OH)]^{2-}$. However, this species exhibits EPR parameters almost identical to those of $[VOA_2H_{-2}]^{4-}$. This monomer $\rightleftharpoons$ tetramer equilibrium, although accompanied by a significant change in bonding mode, cannot be detected by pH-metry as there is no change in the overall protonation state of the molecules. The proton liberated in the hydroxo complex formation process is bound immediately to one of the very strongly basic phenolate groups.

The best fit for the pH-metric titration curves was reached by the assumption of the complexes given in Table 5. Other species, like MA_2 and those indicated in Table 5, were also included but rejected by the computer program during the calculation. The concentration distribution curves for the complexes formed in the copper(II)- and oxo-vanadium(IV)-2,3,4-thba systems are given in Figs. 7 and 8.

In Table 6 the relative stabilities of the mono- and bis-complexes with catecholic co-ordination to Cu^{II} and V^{IV}O are compared for catechol and different catechol derivatives.[3,4,6]

The data in Table 6 are all fairly similar suggesting the same O^-, O^- or $2(O^-, O^-)$ co-ordination in all these systems, with the exception of the corresponding complexes of 2,3-dhba, $[MA_2H_{-2}]^{4-}$, in which case the high stability of the dimer $[M_2A_2H_{-2}]^{2-}$ seems to disfavour the pure $2(O^-, O^-)$ co-ordination.[3,6]

Now, it is also well known that catechol derivatives readily form VA_3-type tris-complexes with catechol and various catechol derivatives. These complexes contain bare six-co-ordinate V^{IV} with a geometry distorted towards trigonal prismatic. It is interesting that these ligands, which are also catecholic derivatives, do not form tris-complexes but only normal oxovanadium(IV) species. The reason for this unusual behaviour is that these ligands can bind oxovanadium(IV) in a salicylate manner too. This bonding mode is favoured at low pH due to the less effective proton competition. Pure catecholate co-ordination is favoured only at higher pH (see speciation curves in Fig. 8), at which, however, the oxygen-displacement reaction $[VO(H_2O)A_2H_{-2}]^{4-} + A^{2-} \rightleftharpoons [VA_3H_{-3}]^{5-} + OH^-$ is rather disfavoured.

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