Proton Electron Nuclear Double Resonance Spectra of Oxovanadium(IV) Complexes formed by Salicylic and *o*-Diphenolic Ligands in Aqueous Solution

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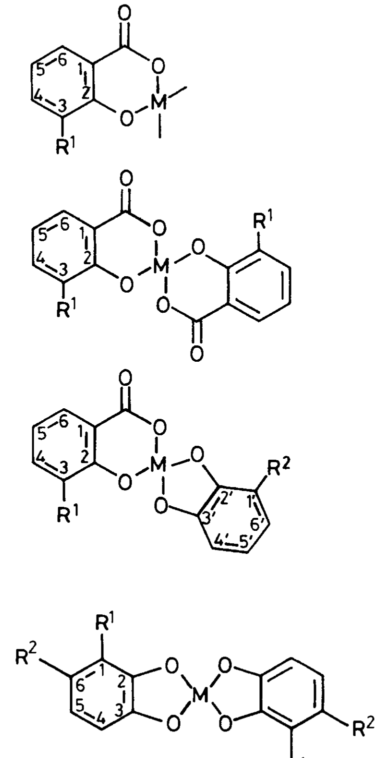
The e.s.r. and ^{1}H electron nuclear double resonance (ENDOR) spectra of oxovanadium(IV) complexes formed in aqueous solution by salicylic and 2,3-dihydroxybenzoic acids have been recorded and compared to those of catecholic ligands previously described. According to both spectroscopies, salicylic acid co-ordinates to the metal ion through the adjacent carboxyl and phenolate donors, while 2,3-dihydroxybenzoic acid behaves as either a catecholic or a salicylic ligand. The ^{1}H ENDOR spectra allowed assignment of the resonances due to the ring protons which are adjacent to metal-bound carboxylate groups and those having contribution from more distant protons. Thus, while the e.s.r. spectra distinguish only the chromophores involved in metal co-ordination, the ENDOR features are distinctive of both the metal surrounding and the ligand structure. The presence of outer-sphere water molecules which, very likely, are hydrogen-bonded to the ligand has also been detected.

Previous ^{1}H electron nuclear double resonance (ENDOR) studies on the oxovanadium(IV) complexes of catecholic ligands and sugars[1,2] showed that the technique may be used to follow the complex-formation properties of the metal ion in aqueous solution. For example, in the case of catecholato complexes,[1] the ENDOR spectra permitted the observation of separate signals due to the interaction of the paramagnetic centre with the aromatic protons, either those adjacent to the co-ordinating groups or even those in more distant positions, as well as with the protons belonging to outer-sphere water molecules.

The successful assignment of the ^{1}H ENDOR features for these systems prompted us to investigate the interaction of the metal ion with less simple ligands, *e.g.* those having two different donors available for chelation, and to identify the individual species formed. We have, therefore, examined the oxovanadium(IV) complexes of salicylic acid as well as those of 2,3-dihydroxybenzoic acid. The latter ligand is a potential donor with either salicylate or catecholate moieties. It is noteworthy that complexes involving the same donor set around the metal ion, and thus exhibiting almost indistinguishable e.s.r. spectra, have been found with these ligands. Therefore, this study has further demonstrated the possibility of ENDOR spectroscopy in distinguishing easily species formed by different ligands even when the same chromophores are involved in the metal co-ordination. The results have been compared to those obtained previously for complexes of *o*-diphenolic ligands,[1] so that the collection of data could be used for the identification of the binding sites in more complex molecules having phenolic donor groups.



Complex	R^1	R^2
(1)	H	
(2)	OH	
(3)	H	
(4)	OH	
(5)	OH	CO_2^-
(6)	H	H
(7)	CO_2^-	H
(8)	H	CO_2^-

Scheme. M = VO

Results

E.S.R. Spectra.—E.s.r. spectra recorded on aqueous solutions, as a function of pH, at either room temperature or 110 K, allowed the main species taking part in complex equilibria to be clearly identified. The spectra showed that salicylic acid first formed a complex with a 1:1 metal-to-ligand molar ratio [complex (1), see Scheme and Table] and then one with a 1:2 ratio [complex (3)]. In both the ligand molecules were chelated to the metal ion through the carboxyl and phenolate groups. The position of the donor groups allowed 2,3-dihydroxybenzoic acid to behave as either a salicylic or *o*-diphenolic chelator, inasmuch as the pH dependence of the e.s.r. spectra indicated that the ligand first co-ordinated to the metal ion with the

Table. E.s.r. and selected ^{1}H ENDOR parameters for oxovanadium(IV) complexes with salicylic and *o*-diphenolic ligands[a]

Complex	g_0	A_0	A_H
(1)	1.967	297.1	1.70 (H^3), 0.95 (H^6)
(2)	1.968	296.2	0.95 (H^6)
(3)	1.975	272.5	1.70 (H^3), 0.95 (H^6)
(4)	1.975	272.5	0.95 (H^6)
(5)	1.972	258.1	1.70 ($H^{4'}$), 0.95 (H^6)
(6)	1.975	245.8	1.80 (H^1, H^4)
(7)	1.972	240.4	1.70 (H^4)
(8)[b]	1.975	247.3	1.80 (H^1, H^4)

[a] The structures of the complexes and proton numbering are illustrated in the Scheme. E.s.r. measurements at ambient temperature, ENDOR measurements at 110 K, A_0 and A_H in MHz. The reported ^{1}H ENDOR couplings are the largest splittings, taken from perpendicular spectra, for the aromatic protons adjacent to co-ordinating groups. [b] Ref. 1.

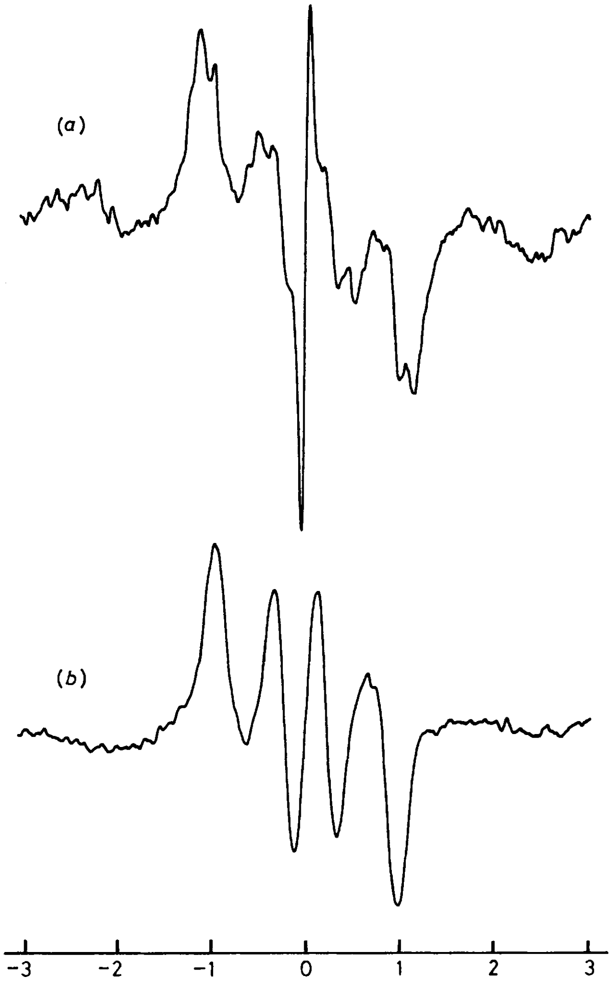


Figure 1. Perpendicular ^{1}H ENDOR spectra of the complex **(6)** in H_2O (*a*) and D_2O (*b*) vp is the free proton frequency

[CO_2^-, O(2)$^-$] donor set and formed complexes **(2)** and **(4)** (see Table). Then, the dissociation of the second phenolic group for one or two ligand molecules resulted in the formation of two further complexes exhibiting mixed salicylato–catecholato [**(5)**, Scheme and Table] and the bis(catecholato) **(7)** co-ordination, respectively. The e.s.r. parameters reported in the Table are distinctive for the complexes formed. In particular, the values of the hyperfine coupling constant fitted well those expected by assuming additive contributions from the individual donors taking part in the in-plane co-ordination.[3] Accordingly, minor spectral differences were detected for the complexes involving the same donor sets.

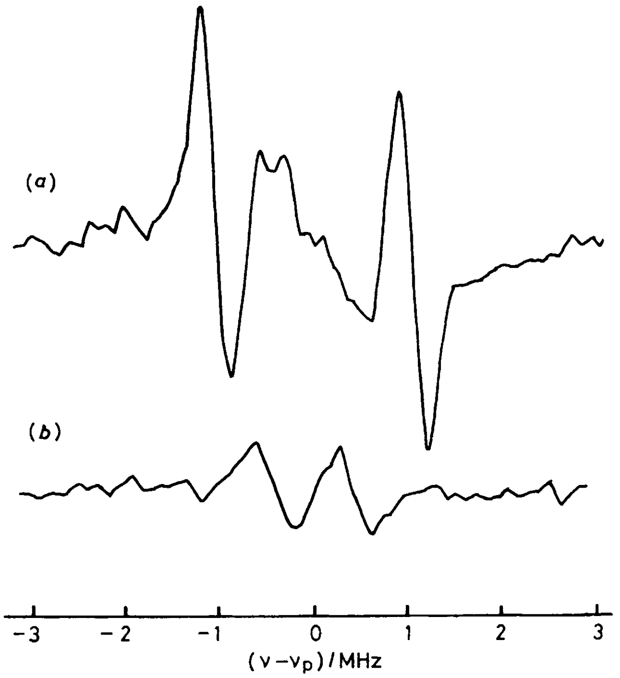


Figure 2. Parallel ^{1}H ENDOR spectra of the complex **(6)** in H_2O (*a*) and D_2O (*b*)

ENDOR Spectra.—According to the theory,[4,5] in the ENDOR spectra of complexes having a tetragonal symmetry a pair of peaks for each set of equivalent protons lying in the *x*, *y* metal plane are expected at $g_{\parallel}$ (or any metal parallel component). Instead, two pairs (one of which is common to both parallel and perpendicular spectra) are expected when observing at $g_{\perp}$ (or any metal perpendicular component). On the other hand, two distinct couples of peaks, one at each orientation of the magnetic field, are expected for the axially located protons.

The ^{1}H ENDOR spectra of the bis(catecholato)oxovanadium(IV) complex **(6)** in H_2O and D_2O are presented in Figures 1 and 2. In water, particularly for the molecular orientation corresponding to the perpendicular field setting, there is a better resolution compared to those reported preliminarily by us.[1] In some cases, due to the rather high modulation values used in order to obtain spectra of reasonable intensity at temperatures as high as 110 K, it was not possible to observe all the expected resonances. However, the main distinguishable superhyperfine (s.h.f.) components for each class of protons were reliably assigned on the basis of a comparative examination of the spectra. The splittings with the coupling of 1.80 MHz were identified as the largest component of protons located in the equatorial plane, namely the aromatic protons adjacent to the phenolate groups. For such protons, because the isotropic contribution to the coupling constant is expected to be small, resonances around 0.90 MHz are expected for the magnetic field aligned along both the parallel and perpendicular directions. These signals are actually distinct in the parallel spectra, but appear only as shoulders in the perpendicular patterns. Analogously, the peaks at 0.40—0.45

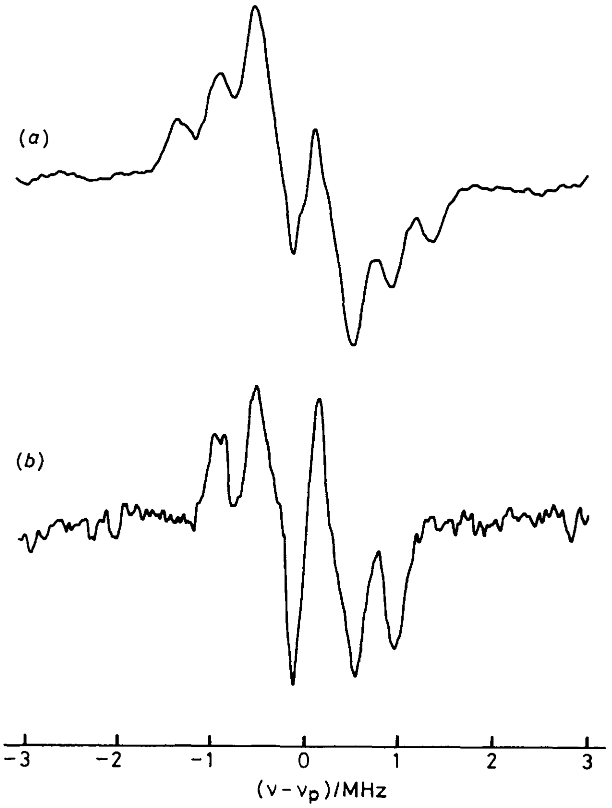


Figure 3. Perpendicular ^1H ENDOR spectra of the complex (3) in H_2O (*a*) and D_2O (*b*)

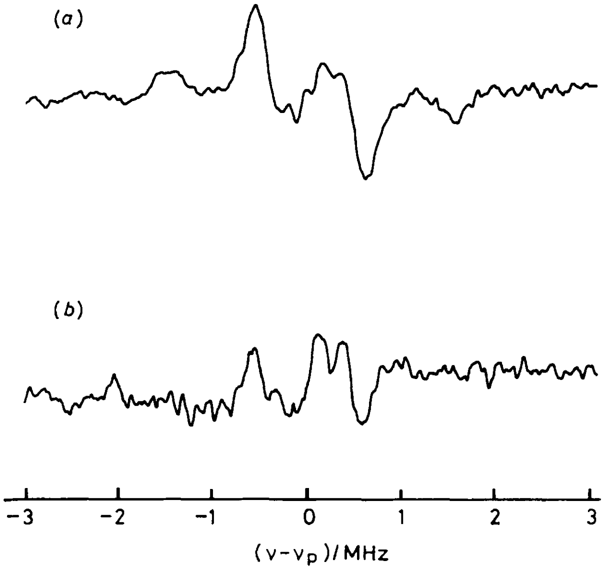


Figure 4. Parallel ^1H ENDOR spectra of the complex (3) in H_2O (*a*) and D_2O (*b*)

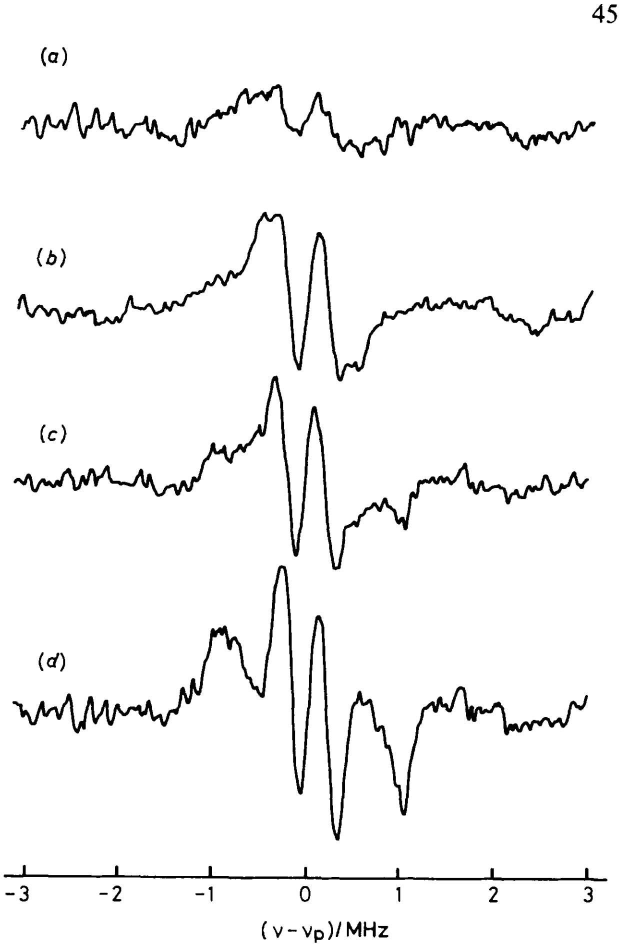


Figure 5. Perpendicular ^1H ENDOR spectra of the 2,3-dihydroxybenzoate complexes in D_2O: (*a*) (**2**), (*b*) (**4**), (*c*) (**5**), and (*d*) (**7**)

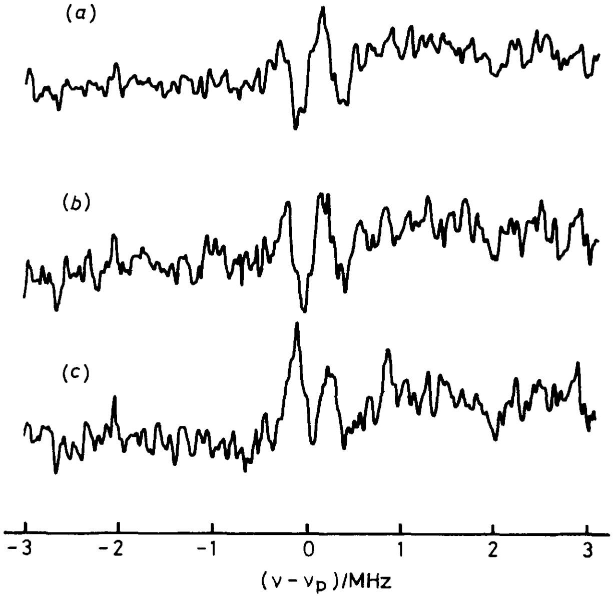


Figure 6. Parallel ^1H ENDOR spectra of the 2,3-dihydroxybenzoate complexes in D_2O: (*a*) (**4**), (*b*) (**5**), and (*c*) (**7**)

MHz which are common to both the parallel and perpendicular spectra may be ascribed to the *meta* ring protons. The largest component of such a class of protons is expected, for the perpendicular field setting, at 0.90—1.00 MHz but it is again overlapped by the nearby resonances.

The ^1H ENDOR pattern which, by comparison between the spectra in H_2O and D_2O, may be attributed to the protons of water consists mainly of peaks at 4.40 and 2.20 MHz, the latter being common to both the parallel and the perpendicular spectra. Thus, the orientation dependence of the splittings is still indicative of protons located in the metal plane.

The ^1H ENDOR spectra recorded for the oxovanadium(IV) complexes of salicylic and 2,3-dihydroxybenzoic acids are shown in Figures 3—8. Both the salicylate species, namely (**1**) and (**3**)

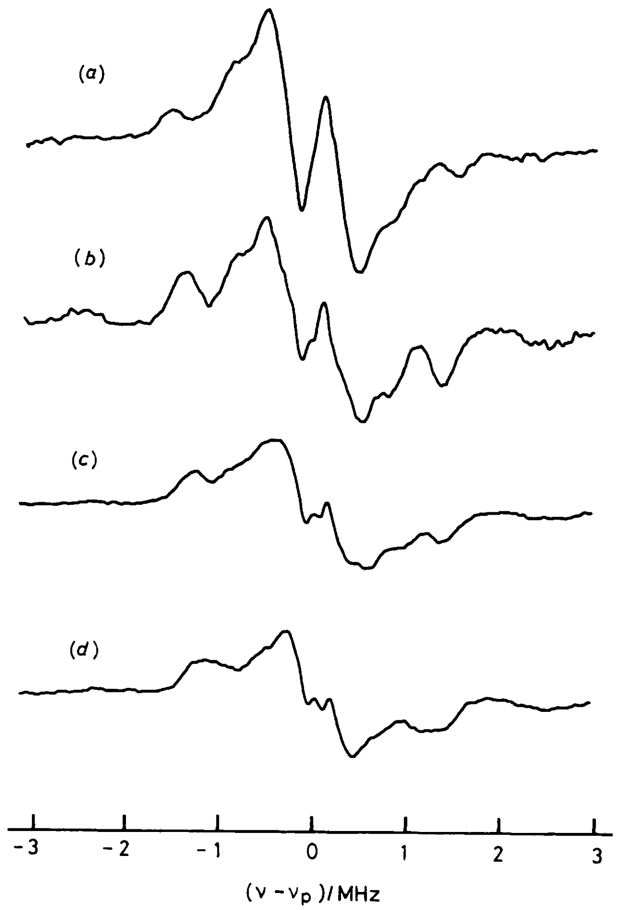


Figure 7. Perpendicular ^1H ENDOR spectra of the 2,3-dihydroxybenzoate complexes in water (*a*) (**2**), (*b*) (**4**), (*c*) (**5**), and (*d*) (**7**)

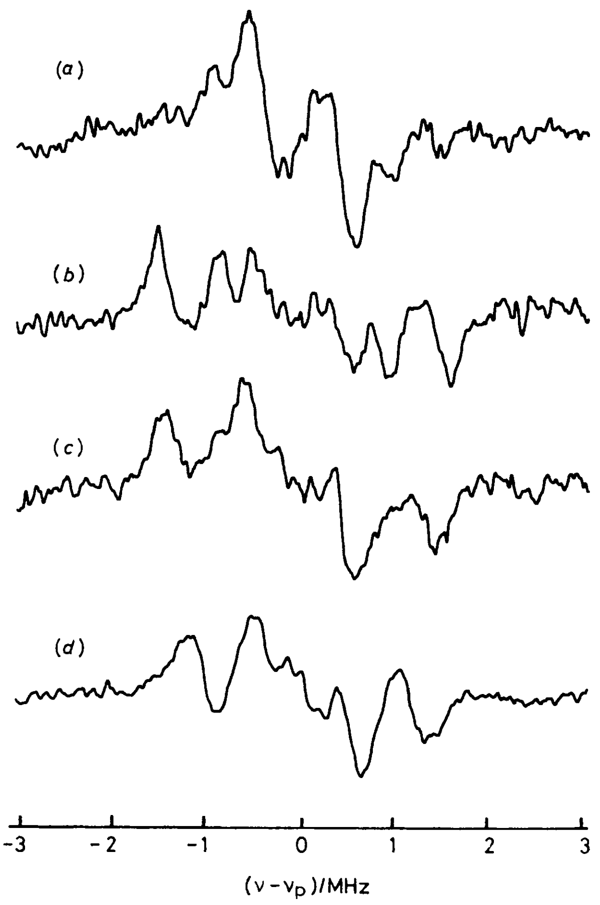


Figure 8. Parallel ^1H ENDOR spectra of the 2,3-dihydroxybenzoate complexes in water: (*a*) (**2**), (*b*) (**4**), (*c*) (**5**), and (*d*) (**7**)

(M:L = 1:1 and 1:2, respectively), yielded essentially identical ^1H ENDOR patterns, although those of the former species were remarkably weaker. The main features in D_2O solution, with the magnetic field set on the perpendicular $M_I = -\frac{3}{2}$ e.s.r. signal, were three pairs of resonances with coupling constants around 1.70, 0.95, and 0.45 MHz, respectively (Figure 3).

The perpendicular field setting for the oxovanadium(IV) 2,3-dihydroxybenzoic acid complexes in D_2O yielded the ^1H ENDOR spectra shown in Figure 5. In this case, both complexes (**2**) and (**4**) adopting the salicylate-type donor set $[CO_2^-, O(2)^-]$ exhibited the coupling constants of 0.95 and 0.45 MHz, the only differences with respect to the corresponding complexes of salicylic acid being the absence of the 1.70-MHz splitting. The latter signal appeared only when complex (**4**) was converted into (**5**) and the co-ordination changed from that of bis(salicylato) into that of mixed salicylato–catecholato. The peak at 0.95 MHz vanished, and that at 1.70 MHz gained in intensity, concomitantly with the further transformation from complex (**5**) into (**7**) and the change from mixed salicylato–catecholato to the bis(catecholato) co-ordination. Therefore, the spectral features of (**7**) were those of the oxovanadium(IV)–catecholato complexes, *cf.* Figure 1, apart from the different intensity ratio between the outer and the inner resonances.

The ^1H ENDOR spectra recorded in D_2O with the field setting on the parallel $M_I = -\frac{5}{2}$ e.s.r. resonance were generally weak [Figures 4(*b*) and 6]. In all cases, however, they showed an envelope of resonances corresponding to couplings between 0.5 and 0.9 MHz, confirming the previous attributions concerning the largest s.h.f. components of the metal–proton interaction.

The spectra recorded on aqueous solutions showed patterns typical of the aqua-ion, which has been widely described,[6–10] as the predominant feature below pH 3. Different signals were observed for the chelated species. The complexes of salicylic acid showed perpendicular resonances at 4.65 and 2.30 MHz and the parallel resonances at 2.50 MHz [Figures 3(*a*) and 4(*a*)] which are again attributable to protons of water molecules lying approximately in the metal plane.

Figures 7 and 8 illustrate the proton ENDOR spectra of the 2,3-dihydroxybenzoic acid complexes. Comparison with the corresponding spectra in D_2O reveals three sets of resonances which may be assigned to protons belonging to water molecules or D_2O-exchangeable groups, *e.g.* phenolic hydroxyls.

All sets of signals exhibit the characteristics expected for protons lying in the metal plane and interacting with the metal through a predominantly dipolar mechanism. The pair with the largest constant is observed in the perpendicular spectra and exhibits a splitting almost twice that for the corresponding components common to both the perpendicular and parallel spectra.

In particular, the set of signals at 4.55, 2.60 (perpendicular) and 2.65 (parallel) MHz, appearing in the spectra of complex (**4**), are almost the same as those observed for the complexes of salicylic acid. Analogously, the resonances at 4.4 MHz (appearing in the perpendicular spectra as broad peaks) and 2.2 MHz (common to perpendicular and parallel spectra) are analogous to those of the complex of catechol. Thus, the two above sets are attributable to protons of water molecules hydrogen-bonded to the 2,3-dihydroxybenzoate ligand co-ordinating through the salicylato and catecholato moieties respectively.

The third set of resonances consists of the parallel and perpendicular signals at 1.60 MHz [Figures 7 and 8, spectra (*a*) and (*b*)] and the perpendicular component at 2.95 MHz, which is clearly observable in Figure 7(*a*), but overlapped by the resonance at 2.60 MHz in Figure 7(*b*). This set vanishes when the ligand becomes fully deprotonated. Thus, it may be assumed as due to the hydrogen atom of the undissociated phenolic groups at the C(3) atom. Such a proton is very likely shared with the vicinal $O(2)^-$ oxygen atom and is thus located nearby the vanadium atom in the *x*, *y* plane.

Discussion and Conclusions

The comparative examination of the results shows that the most distinctive ^1H ENDOR characteristics of the systems studied are those appearing in the spectra recorded in D_2O with the magnetic field set on the perpendicular E.S.R. resonances. The dominant features of these spectra are the signals with the largest coupling constants of 0.95 and 1.70 MHz for the complex with salicylic and 2,3-dihydroxybenzoic acid, and 1.80 MHz for catechol (Table). The coupling constant of 1.80 MHz was previously assigned by us,[1] using the crystallographic data available for the potassium bis(catecholato)oxovanadate(IV) complex.[11] Under the assumption of a purely dipolar metal–proton interaction and coaxial *g* and proton tensors, this value is in fairly good agreement with the largest of the s.h.f. components expected for the metal interaction with the aromatic protons in the *ortho* position to the phenolate group (metal–proton distance of *ca.* 0.44 nm). Because an interaction of similar extent is expected between the metal ion and the proton on the C(3) atom in the complexes of salicylic acid, the above attribution may be extended also to the pair at 1.70 MHz. On the other hand, the signals with the 0.95-MHz coupling, which are absent in the spectra of complexes with pure phenolate co-ordination and are peculiar to the oxovanadium(IV)-salicylic acid system, may be ascribed to the aromatic proton which is adjacent to the carboxylate group. Thus, while the co-ordination of catechol results in the 1.80-MHz coupling due to the interaction with the aromatic protons adjacent to the donor atoms, the co-ordination of salicylate to vanadium is distinguished by two pairs of signals at 1.70 and 0.95 MHz, as a consequence of the non-equivalence of the protons closest to the co-ordinating groups.

This interpretation is confirmed by the spectral trend observed for the 2,3-dihydroxybenzoic acid system. In this case the signals at 0.95 MHz are distinguished in the perpendicular spectra, while those at 1.70 MHz are absent, when the ligand co-ordinates exclusively through the carboxylate and 2-phenolate groups. This is a clear evidence for the presence of a substituent (the second phenolic group) at the C(3) atom. Accordingly, the signal at 1.70 MHz appears only concomitantly with the formation of complex (**5**). Indeed, in this complex one of the bound ligands retains a salicylate-like donor set and yields a coupling of 0.95 MHz. The second ligand, adopting a catecholate-type co-ordination, is, instead, responsible for the 1.70-MHz couplings which are indicative of the presence of a proton, that on the C(4) atom, adjacent to the bound phenolate groups. The complete replacement of carboxylate by phenolate donors in the vanadium co-ordination removes the signal at 0.95 MHz, indicating that the protons on the C(6) atoms are no longer adjacent to metal-bound groups. Consequently, the observation of the signal at 1.70 MHz for the final 2,3-dihydroxybenzoate complex, which is of the bis(catecholato)-type is explainable by the interaction of vanadium with two protons, those on C(4), adjacent to co-ordinating groups.

The above interpretation is supported by theoretical considerations. With the same approximations described above (dipolar interaction and coaxial *g* and s.h.f. tensors), by considering the 0.95-MHz coupling as the largest component of the metal–proton interaction, one calculates a distance of *ca.* 0.55 nm for the proton adjacent to the co-ordinating carboxyl group in salicylic acid. This value compares well with that predicted for a salicylate complex by use of molecular modelling. The other components for the same proton are expected to be -0.47 and -0.47 MHz, respectively, and they cannot be distinguished because of overlapping with other components in the central part of the spectra. The couplings with the remote aromatic protons are expected in the same range, *e.g.*, 0.70, -0.35, and -0.35 MHz for the hydrogen atoms in the *meta* position to the phenolate group (r = *ca.* 0.60 nm).

As to the signal from water molecules, the pattern observed for the catechol complexes indicates that the protons are located in the metal plane. By using again the point-dipole approximation, a distance of *ca.* 0.33 nm from vanadium is calculated for these protons. Therefore, the protons of water molecules hydrogen-bonded to the phenolate groups are, very likely, those responsible for the ^1H ENDOR spectra. The same attribution is valid for the complexes of salicylic acid where also hydrogen-bonding interactions with the carboxylate oxygen are conceivable. The presence of outer-sphere water molecules, hydrogen-bonded to the donor groups, has been detected also for the 2,3-dihydroxybenzoate species. However, the broadness of the bands, particularly those for complexes (**5**) and (**7**), are suggestive of a more complicated situation.

The interaction between the metal ion and the hydrogen atom belonging to the undissociated phenolic group of the 2,3-dihydroxybenzoate ligand co-ordinating in a salicylic-like mode is supported by several arguments. With similar ligands, the possibility of an intramolecular hydrogen-bonding interaction between a phenolic hydroxyl and a vicinal negatively charged group, *e.g.* carboxylate, was previously substantiated by the distinct increase in the corresponding p*K* value.[12] Furthermore, the set of resonances observed points to a proton–metal distance of *ca.* 0.37 nm, which is in good agreement with that predicted by an examination of molecular models. Finally, it is very significant that the decrease in intensity of these resonances is concomitant with the appearance of signals attributable to the proton on the C(4) atom. This is just the spectral trend expected as the result of the rearrangement consequent upon deprotonation and co-ordination of the phenolic group, namely the coupling due the D_2O-exchangeable hydrogen is replaced by that with the aromatic proton vicinal to the co-ordinated group.

Experimental

Materials.—Salicylic and 2,3-dihydroxybenzoic acids, purchased from Aldrich, were used after recrystallization from water. Catechol (Sigma) was recrystallized from benzene. The salt $VO(SO_4)\cdot 3H_2O$ was obtained from Aldrich. Fresh solutions (2×10^{-2} mol dm^{-3} VO^{2+}, ligand-to-metal molar ratios from 1:1 to 5:1) were prepared in twice distilled water (or 99.9% D_2O, Carlo Erba), just prior to the commencement of any experiment. The ionic strength was 0.1 mol dm^{-3} ($KClO_4$). In order to minimize air oxidation of oxovanadium(IV), nitrogen was run through the solutions during preparation and titrations. The pH (pD) was adjusted by addition of H_2SO_4 (D_2SO_4, 99.5% D) and NaOH (NaOD, 99.8% D); pD = pH meter reading + 0.4.[13] Dimethyl sulphoxide [$(CD_3)_2SO$, 99.5% D] was added to samples to ensure good glass formation.

Measurements.—E.s.r. and ^1H ENDOR measurements were carried out on a Bruker 220 D instrument operating at *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 field on the parallel $M_I = -\frac{5}{2}$ or perpendicular $M_I = -\frac{3}{2}$ e.s.r. resonances.

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