

Proton Electron Nuclear Double Resonance Study of Oxovanadium(IV) Complexes of *o*-Diphenolic Ligands

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The vanadium(IV) complexes of catechol, 3,4-dihydroxybenzoic acid, and naphthalene-2,3-diol, in water or D₂O solution, have been studied by ¹H electron nuclear double resonance (ENDOR) spectroscopy at 110 K. The spectra show prominent peaks which are due to ring protons adjacent to metal-bound phenolate groups, together with resonances which have contributions from more distant protons. On the whole, the ¹H ENDOR patterns of the studied complexes may be satisfactorily assigned using the structural data for potassium bis(catecholato)oxovanadate(IV) and thus may be considered as diagnostic of vanadium(IV)-phenolate co-ordination. The presence of outer-sphere water molecules has also been detected in aqueous solution.

Phenolic groups take part in the metal binding site in many biologically active molecules, *e.g.* transferrin and enterobactin, or naturally occurring polymeric compounds, *e.g.* humic and fulvic acids. The e.s.r. properties of oxovanadium(IV) make this ion an excellent spectroscopic probe for the identification of phenolate co-ordination. However, in the absence of superhyperfine splitting, the pertinent information may be limited just to the set of metal-surrounding donor atoms. Electron nuclear double resonance (ENDOR) spectroscopy is a powerful technique which, by detecting the interaction between paramagnetic ions and ligand nuclei, even those more distant than the donor atoms, may provide information also on the structure of ligands. While this technique is increasingly used to probe the structure of metal complexes,¹⁻¹³ corresponding studies on complexes involving metal-phenolate bonds are still lacking, in spite of the wide interest in these models in bioinorganic chemistry. We have therefore undertaken an ENDOR study of vanadium(IV) complexes formed in aqueous solution by simple ligands bearing phenolic groups, in order to check whether ENDOR spectra could be a spectroscopic tool useful for assigning the ligand structure, when similar chromophores are involved. The results obtained for the complexes of some *o*-diphenolic ligands, catechol (benzene-1,2-diol), 3,4-dihydroxybenzoic acid, and naphthalene-2,3-diol are reported here. Other phenolic systems will be examined in the future, the final goal being the assignment of ENDOR features of vanadium(IV) phenolate complexes and the possible application of the technique for a more complete elucidation of the vanadium(IV) binding sites in complex biological systems which are still a matter of debate.

Results

E.S.R. Spectra.—E.s.r. spectra recorded on aqueous solutions, at various pH values either at room temperature or at 110 K allowed the species taking part in complex equilibria to be identified. The spectral trend was similar with the different ligands and it was consistent with the usual behaviour of the *o*-diphenolic ligands.¹⁴ As the pH was increased, at first the complexes with a 1:1 metal-to-ligand ratio (ML) and then those with a 1:2 metal ratio (ML₂), both involving ligands chelating through the *o*-diphenolate moiety, were observed. The e.s.r. parameters were not significantly different for the different

Table. E.s.r. and ¹H ENDOR parameters for oxovanadium(IV) complexes with *o*-diphenolic ligands in water or D₂O solution^a

Ligand	M:L	E.s.r.		¹ H ENDOR ^b
		<i>g</i> ₀	<i>A</i> ₀	
Catecholate	1:1	1.968	286.9	1.8, 0.4
	1:2	1.975	245.8	1.8, 0.4
3,4-Dihydroxybenzoate	1:1	1.970	286.6	1.8, 0.4
	1:2	1.975	247.3	1.8, 0.4
Naphthalene-2,3-diolate	1:1	1.968	286.9	^c
	1:2	1.975	245.8	1.8, 0.4

^a E.s.r. measurements at ambient temperature, ENDOR measurements at 110 K; *A*₀ and *A*_H in MHz. ^b Couplings taken from spectra recorded with the field set on the perpendicular *M*_I = −³/₂ e.s.r. resonance. ^c Not detected.

systems (Table), indicating a common stereochemistry, due to the similarity of the co-ordinating properties of the ligands.

ENDOR Spectra.—Proton ENDOR measurements with the magnetic-field setting on the perpendicular *M*_I = −³/₂ resonance of the e.s.r. spectra of the complexes ML and ML₂ in D₂O solution are reported in Figure 1. Essentially identical ¹H ENDOR patterns were observed, regardless of the nature of the ligands and the composition (M:L = 1:1 or 1:2) of the complex species, except for the intensity ratio of the components. The main features of the spectra were two pairs of resonances, with coupling constants around 1.8 and 0.4 MHz, respectively (Table).

The ENDOR spectra recorded by setting the magnetic field on the parallel *M*_I = −⁵/₂ e.s.r. resonance were generally weak (Figure 2) and, in all cases, exhibited ill resolved resonances accounting for couplings over the range 0.4–0.8 MHz.

When the spectra were recorded on aqueous solutions, Figure 3, the spectral features were again the same for the different systems. In all cases, the spectrum typical of the aqua-ion, which has been widely described in the literature,¹⁰⁻¹⁴ was predominant at pH below 4. In the presence of extensive complex formation, the signals due to protons of water (couplings of 4.4 and 2.2 MHz in the perpendicular spectra, and 2.2 MHz in the

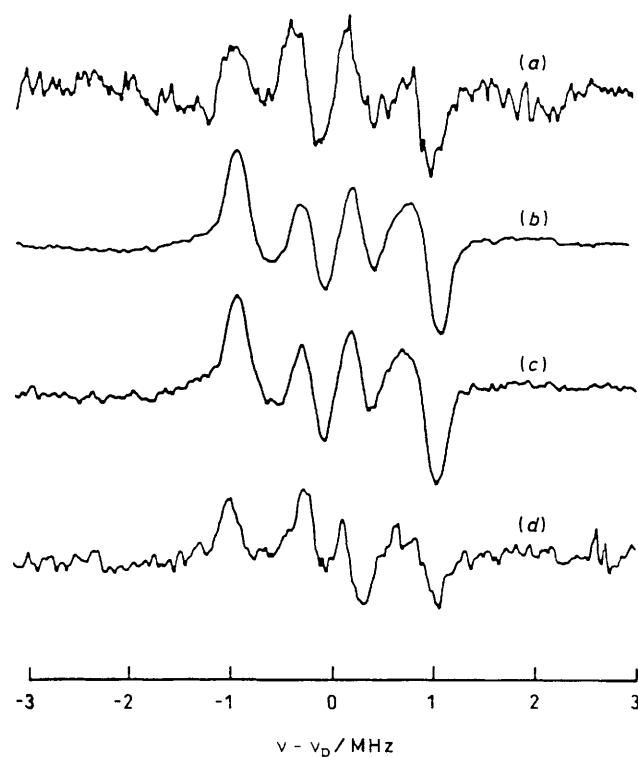


Figure 1. Perpendicular proton ENDOR spectra of vanadyl complexes in frozen D_2O solution: (a) catechol ($M:L = 1:1$); (b) ($M:L = 1:2$); (c) 3,4-dihydroxybenzoate ($M:L = 1:2$); and (d) naphthalene-2,3-diolate ($M:L = 1:2$)

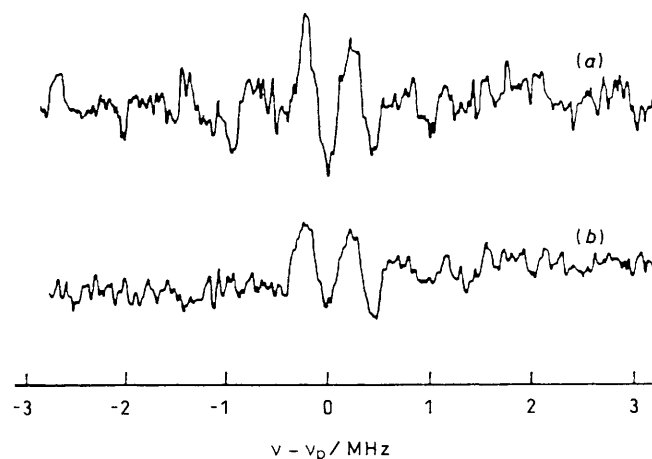


Figure 2. Parallel 1H ENDOR spectra of vanadyl complexes in frozen D_2O solution: (a) catechol ($M:L = 1:2$); (b) 3,4-dihydroxybenzoate ($M:L = 1:2$)

parallel spectra) were observed. However, weak contributions in the central part of the spectra, even due to matrix effects, cannot be excluded.

Discussion and Conclusions

The experimental results substantiate that the ENDOR features of the studied systems are distinctive enough and may be considered as diagnostic of VO^{IV} -phenolate co-ordination when protons are present in close proximity to the metal binding site. The observed trend clearly indicates that the perpendicular couplings of about 1.8 MHz may be assigned to aromatic

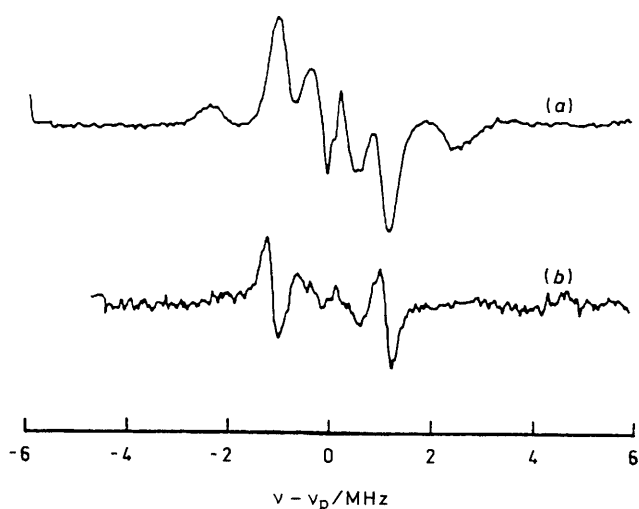


Figure 3. Perpendicular (a) and parallel (b) 1H ENDOR spectra of the vanadyl catechol complex ($M:L = 1:2$) in frozen aqueous solution

protons adjacent to metal-bound phenolate groups. Instead, couplings around 0.4 MHz may have contributions from protons which are more distant.

As the g anisotropy dominates the e.s.r. spectra of oxovanadium(IV), crystal-like ENDOR spectra may be obtained from e.s.r. powder patterns. According to theory,¹⁵ for complexes with tetragonal symmetry, a pair of ENDOR peaks for each set of equivalent protons lying in the metal plane is expected at g_{\parallel} (or any metal parallel component), while two pairs of peaks, reflecting the anisotropy of the metal-proton interaction, are expected when observing at g_{\perp} (or any metal perpendicular component). If the interaction between protons and unpaired electron of vanadium may be assumed to be purely dipolar in origin, the magnitudes of these splittings are proportional to r^{-3} , where r is the vanadium-proton distance.¹⁶

The crystallographic data available for the complex potassium bis(catecholato)oxovanadate(IV)¹⁷ may be used to evaluate the expected coupling constants for the complex by assuming coaxial g and proton tensors. In this case one calculates coupling constants of +1.72, -0.86, and -0.86 MHz for the aromatic protons in *ortho* position to the phenolate group ($r = ca. 0.44$ nm), while values of +0.71, -0.35, and -0.35 MHz are expected for the protons in *meta* position ($r = ca. 0.60$ nm). These calculations are in fair agreement with the experimental data if one assumes that the largest and the smallest couplings (1.72 and -0.35 MHz) are the predominant features of the perpendicular spectrum, while the intermediate couplings (0.71 MHz) are the weak shoulders distinguishable near the 0.4-MHz peaks. On the other hand, due to the poor quality of the observed spectra, the peaks at -0.35 and -0.86 MHz are not resolved in the parallel patterns.

Finally, by using the same approximation described above, the proton coupling of the water molecules, which very likely are hydrogen-bound to the phenolic oxygens, may be used to calculate the metal-proton distance. In this case a value of 0.32 nm is obtained.

Experimental

Materials.—Catechol, 3,4-dihydroxybenzoic acid, and naphthalene-2,3-diol were purchased from Aldrich and used without further purification. The salt $VO(SO_4) \cdot 3H_2O$ (Aldrich) was the metal source. Fresh solutions (2×10^{-2} mol dm^{-3} VO^{2+} , ligand-to-metal molar ratio 2:1) were prepared in twice distilled water (or 99.9% D_2O , Carlo Erba), just prior to the

commencement of any experiment. 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 H₂SO₄ (D₂SO₄, 99.5% D) and NaOH (NaOD, 99.8% D); pD = pH meter reading + 0.4. [D₂H₆] Dimethyl sulphoxide (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 the X-band frequency (ca. 9.40 GHz) equipped with a Bruker ENDOR accessory. Instrumental settings: microwave power 50 mW; radiofrequency power at 14 MHz, 100 W; frequency modulation depth 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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