# Stabilization of the Open-chain Structure of D-Galacturonic Acid in a Dimeric Complex with Oxovanadium(IV)

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The formation of a dimeric $VO^{IV}$–D-galacturonic acid complex in aqueous solution has been studied by spectroscopic methods, namely e.s.r., electron nuclear double resonance, and electronic absorption. The complex exhibits properties consistent with a metal–metal distance of about 5.0 Å, which is very similar to that found in the well known $VO^{IV}$–tartrate dimers. The only way to accommodate the metal ions at such a distance and to fit the spectroscopic data is to assume that the ligand co-ordinates to the metal ion through the $CO_2^-$, $O(4)^-$ and $O(3)^-$, $O(2)^-$ donor sets and adopts an open-chain structure which is stabilized by the dimer complex formation.

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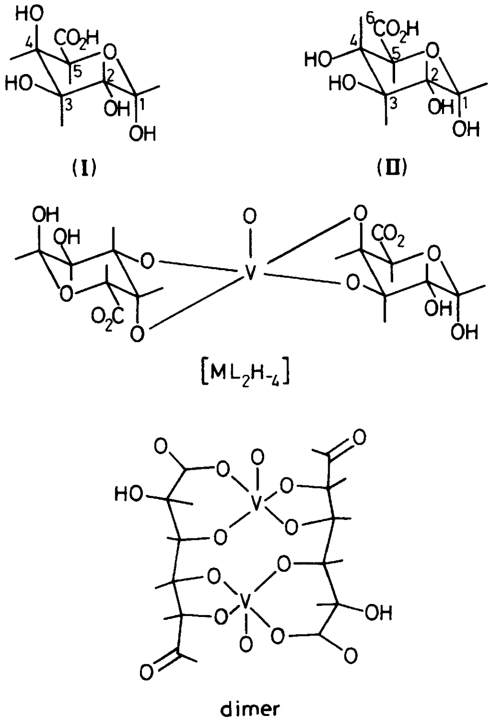
In previous papers we presented potentiometric and spectroscopic studies on the interaction of $VO^{IV}$ with D-galacturonic and D-glucuronic acids [(I) and (II), see Scheme].[1,2] It was found that both these sugars are effective ligands toward oxovanadium(IV) ions.

In particular, with D-galacturonic acid (HL), the carboxylate group initiates the co-ordination at pH 3 to yield $[ML_2]$ complexes with the ligand deprotonated at the carboxyl group. One or two sugar hydroxyl groups, those at the $C^4$ and $C^3$ atoms, are then deprotonated and involved in the co-ordination. Mononuclear complexes with the dinegative $LH_{-1}$ and trinegative $LH_{-2}$ anions, *e.g.* $[ML_2H_{-2}]$ and $ML_2H_{-4}]$, are thus formed. At high pH, however, the e.s.r. and electron nuclear double resonance (ENDOR) spectra of the more concentrated solutions containing $VO^{IV}$ and D-galacturonic acid provided evidence for the formation of a new species which was clearly of the dinuclear type. While in the monomeric species there is no need to assume that the structure of the ligand is different from the closed one, which is stable for the free ligand, all the data for the dimer suggested instead the adoption of an open form. Thus the full characterization of this species and the assignment of its structure appeared to be of interest for several reasons. First, there are only a limited number of reports, mostly on tartrates,[3–8] concerning the formation of dinuclear vanadium(IV) species in solution. Secondly, the ability of sugars to form polynuclear complexes using most of their hydroxyl groups in co-ordination is still unknown. Finally, the adoption of the open-chain form by a sugar upon complex formation is rather unusual and it would undoubtedly be a factor affecting the function and the reactivity of the ligand in biological systems.



**Scheme.**

## Results and Discussion

E.s.r. spectra recorded at room temperature on the $VO^{IV}$–D-galacturonic acid system in basic solutions are presented in Figure 1. The spectrum obtained for a ligand excess as high as 5:1 [Figure 1(*a*)] resembles closely that assigned as the oxovanadium(IV) ion bound to two sugar molecules *via* four deprotonated hydroxyl groups (species $[ML_2H_{-4}]$ in the Scheme).[1,2] A decrease in the ligand excess, however, leads to a drastic modification of the spectrum, as seen in Figure 1(*b*) and (*c*). The most resolved and homogeneous pattern of this type is observed for solutions containing equimolar amounts of metal ions and ligand. This could suggest that the species responsible for the e.s.r. spectrum in Figure 1(*b*) and (*c*) is an equimolar oxovanadium(IV) galacturonate complex. Also the e.s.r. spectra obtained at low temperatures (Figure 2) depend critically on the ligand to metal molar ratio. The spectrum shown in Figure 2(*b*) contains some traces of the monomeric species shown in the Scheme [see Figure 2(*a*)] but it differs completely from all spectra obtained earlier for the $VO^{IV}$–D-galacturonate system.[1,2] The spectra shown in Figure 1(*b*) and (*c*) as well as that presented in Figure 2(*b*) are characteristic for the dimeric

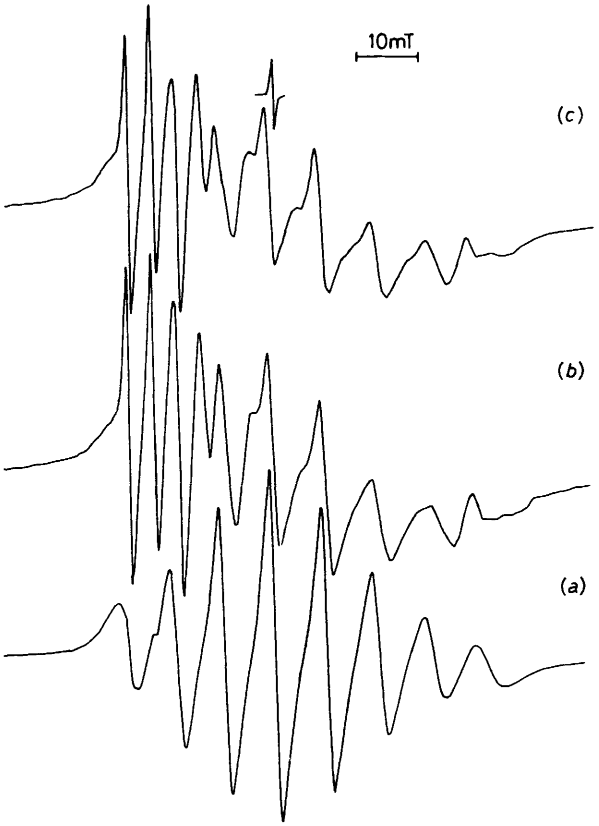


**Figure 1.** Room-temperature e.s.r. spectra of the VO$^{IV}$–D-galacturonic acid system at pH 10.8: M:L = 1:5 (*a*), 1:2 (*b*), or 1:1 (*c*). The oxovanadium(IV) concentration was $2 \times 10^{-2}$ mol dm$^{-3}$ for spectrum (*a*) and $4.8 \times 10^{-2}$ mol dm$^{-3}$ for (*b*) and (*c*)

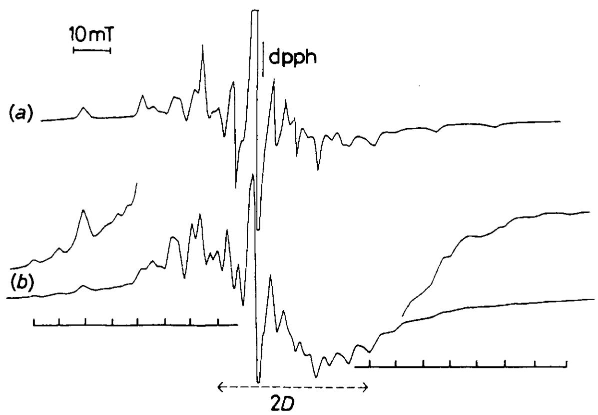


**Figure 2.** E.s.r. spectra recorded at 110 K for the VO$^{IV}$–D-galacturonic acid system at pH 10.8: M:L = 1:5 (*a*) or 1:1 (*b*). Oxovanadium(IV) concentration as in Figure 1; dpph = diphenylpicrylhydrazyl

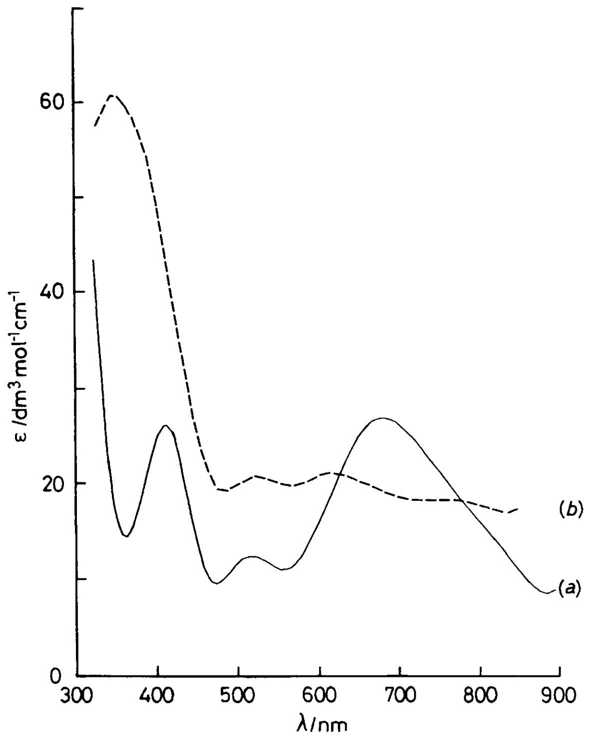


**Figure 3.** Electronic spectra of the VO$^{IV}$–D-galacturonic acid system at pH 10.8; details as in Figure 2

species, as previously found for complexes with several tartrate and porphyrin ligands.[3–8] The characteristic feature of the isotropic spectra is the appearance of fifteen hyperfine components, due to the interaction of the unpaired electron with two equivalent vanadium atoms ($I = \frac{7}{2}$), exhibiting a splitting constant which is almost half that observed for the monomeric species. In the frozen-solution spectrum each of the perpendicular and parallel eight-line patterns is decomposed into two sets of fifteen components. The separation is *D*, the zero-field parameter, between the perpendicular sets and 2*D* for the parallel sets. The positions of the outer components of the two fifteen-line parallel patterns are shown in the stick diagram in Figure 2. By analysis of the patterns of resonances for the dimer the following parameters could be calculated: $\langle g \rangle = 1.975$ and $\langle A \rangle = 37.9 \times 10^{-4}$ cm$^{-1}$ from the room-temperature spectra and $g_{\parallel} = 1.946$, $A_{\parallel} = 73.6 \times 10^{-4}$ cm$^{-1}$, and $2D = 390 \times 10^{-4}$ cm$^{-1}$ from the frozen-solution one (110 K). The evaluation of the distance between the two oxovanadium(IV) ions from *D* (assuming a purely dipolar interaction in an axially symmetric dimer[5]) yields a value around 5.0 Å which is close to those found by *X*-ray structure determination for oxovanadium(IV) dimeric complexes with tartaric acid analogues as well as porphyrins.[4,6] Also the absorption spectra, which are distinctly different for the monomeric and the dimeric species, indicate the formation of a dinuclear complex as shown in Figure 3. Unlike the monomeric species, *e.g.* [$ML_2H_{-4}$], the dimeric species exhibits four absorption bands similar to those recorded for other well established dimers.[3–7]

A further indication of the formation of a dimeric species comes from the examination of the ENDOR spectra. From Figure 4(*b*), in the pH range where this dimeric species exists, a line, remarkably narrower than the others, appears at the free-proton frequency even in $D_2O$ solution. The same feature is observed in the case of dimeric vanadium(IV) tartrate [Figure 4(*c*)], but is absent in systems containing only monomeric species {*e.g.* [$ML_2H_{-2}$], Figure 4(*a*)}. This band gains intensity with increasing dimer concentration; also it is always the most intense peak even when the monomeric species [$ML_2H_{-4}$] is largely predominant [see Figure 4(*d*) in ref. 2]. The attribution of this anomalous peak remained unexplained in our previous work.[2] The discovery of the dimeric species in this study has allowed us to clarify the nature of the band and to attribute it to the presence of magnetically interacting nuclei, analogously as in the case of the biradicals in the triplet state.[9] The peculiar narrowness and intensity of the resonance are also in accord with theoretical predictions.[10]

The results presented here clearly indicate the formation of a

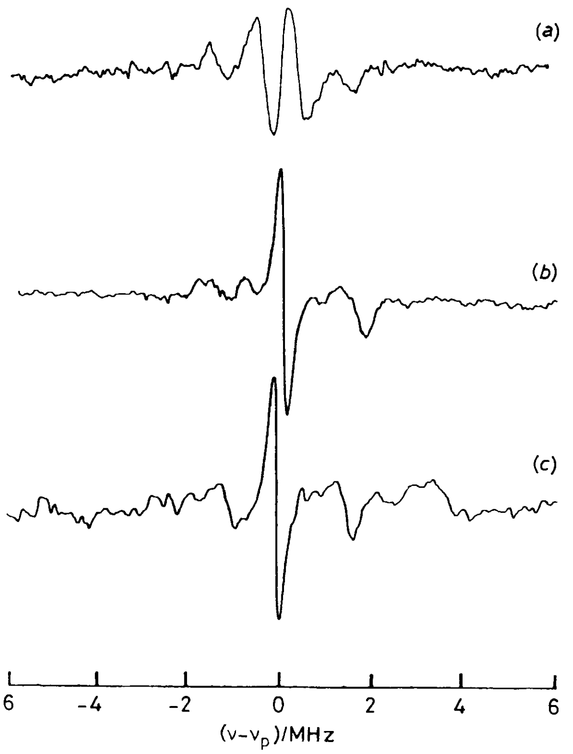


**Figure 4.** Perpendicular proton ENDOR spectra recorded on frozen $D_2O$ solutions: (a) $VO^{IV}$–galacturonic acid system $[ML_2H_{-2}]$ (M:L = 1:2) at pD 7.5, (b) as (a) but M:L = 1:1 at pD 10.5, and (c) $VO^{IV}$–tartaric acid system (M:L = 1:1) at pD 7.8. The oxovanadium(IV) concentration is $2 \times 10^{-2}$ mol dm$^{-3}$ for spectrum (a) and $4 \times 10^{-2}$ mol dm$^{-3}$ for (b) and (c)

dimeric species in the $VO^{IV}$–D-galacturonic acid system. Since the excess of ligand favours the 1:2 (metal to ligand) species described earlier,[1,2] the dimeric complex actually studied is most likely an equimolar species. The close similarities of the spectroscopic data for the studied dimer to those reported previously with *e.g.* tartaric acid and the fact that in both cases the dimeric form is an equimolar complex suggest also that the corresponding structures should be similar to each other. Having all the above indications in mind, molecular models were examined. The two oxovanadium(IV) square-pyramidal monomeric units can easily be arranged at the distance evaluated above but only if the sugar ligand is in its open-chain structure. There are no steric possibilities of forming a dinuclear complex with the closed structure of the sugar ligand unless $OH^-$ groups are assumed to bridge the two oxovanadium(IV) ions. However, these kinds of dimers are e.s.r. silent, see *e.g.* ref. 1, and exhibit a metal–metal distance considerably shorter than that substantiated in the present case. A further support of the assignment of the structure comes from the observation that a similar dimeric complex is not formed with D-glucuronic acid. Because the ligands differ only in the position of the substituents on $C^4$ it is easy to infer that the deprotonated hydroxyl group on $C^4$ is involved in metal binding with D-galacturonic acid, while it is in an unfavourable position in the case of D-glucuronic acid. On these bases, the only possible resulting dimeric structure is that presented in the Scheme.

For sugars, usually the abundance of the open-chain form is very low ($\ll 1\%$) compared to the two closed anomeric α and β forms. In the present case the reason for the stabilization of the open-chain form is undoubtedly the fact that in a 1:1 (metal:ligand) complex with the closed form only two of the carboxyl or hydroxyl groups of the ligand are available for co-ordination to the metal. Instead, the open-chain form behaves as an analogue of tartaric acid and, as such, can yield dimeric species of comparable stability.[8] Therefore, the open-chain form, being a more effective complexing agent than the closed one, can be stabilized. Electronic effects originating from the co-ordination of the metal ion to the sugar in the pyranosic form could be additional factors favouring the opening process.

## Experimental

*Materials.*—D-Galacturonic acid monohydrate was a commercial sample (Fluka); $VO(SO_4)\cdot3H_2O$ (Aldrich) was used as the metal-ion source. Fresh solutions of $VO^{2+}$ were prepared just prior to the spectral measurements. In order to minimize oxidation of oxovanadium(IV) ions in the air, nitrogen or argon was bubbled through the solutions during preparation and titrations.

*Spectroscopic Measurements.*—Electron spin resonance measurements were carried out on a Varian E-9 spectrometer at the *X*-band frequency (9.15 GHz) at room temperature and at 110 K, using flat quartz cells sealed under nitrogen. Dimethyl sulphoxide was added to ensure good glass formation in frozen solution. Proton ENDOR measurements were carried out at 110 K on a Bruker 220 D spectrometer operating at 9.4 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. The spectra were recorded on frozen $D_2O$ solutions by setting the magnetic field on one of the perpendicular e.s.r. resonances. The electronic spectra were recorded with a Beckman model 25 spectrophotometer. The oxovanadium(IV) concentration used was about 0.048 mol dm$^{-3}$ and the metal to ligand molar ratio ranged from 2:1 to 1:5.

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## References

1 G. Micera, A. Dessì, H. Kozłowski, B. Radomska, J. Urbanska, P. Decock, B. Dubois, and I. Olivier, *Carbohydr. Res.*, 1989, **188**, 25.
2 M. Branca, G. Micera, A. Dessì, and H. Kozłowski, *J. Chem. Soc., Dalton Trans.*, 1989, 1283.
3 R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 1967, **6**, 735.
4 V. Thanabal and V. Krishnan, *Inorg. Chem.*, 1982, **21**, 3606.
5 R. L. Belford, N. D. Chasteen, H. So, and R. E. Tapscott, *J. Am. Chem. Soc.*, 1969, **91**, 4675.
6 S. H. Hahs, R. B. Ortega, R. E. Tapscott, Ch. F. Campana, and B. Morosin, *Inorg. Chem.*, 1982, **21**, 664.
7 R. M. Holland and R. E. Tapscott, *J. Coord. Chem.*, 1981, **11**, 17.
8 L. D. Pettit and J. L. M. Swash, *J. Chem. Soc., Dalton Trans.*, 1978, 286.
9 H. D. Brauer, H. Stieger, J. M. Hyde, L. D. Kispert, and G. R. Luckhurst, *Mol. Phys.*, 1969, **17**, 457.
10 B. Kirste, H. van Willigen, H. Kurreck, K. Möbius, M. Plato, and R. Biehl, *J. Am. Chem. Soc.*, 1978, **100**, 7505.

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