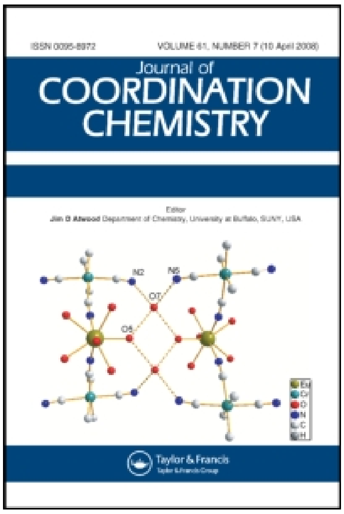

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VANADYL(IV) COMPLEXES OF LACTOBIONIC ACID: POTENTIOMETRIC AND SPECTROSCOPIC STUDIES

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Potentiometric and spectroscopic studies have shown that in the VO(IV)-lactobionic acid system five different species are involved in coordination equilibria. All complexes consist of one metal ion and two ligand molecules. Stability constants for the vanadyl complexes with lactobionic acid are considerably higher than those for uronic acids, although the donor atoms involved in metal ion coordination are exactly the same. The main reason for the higher stability of lactobionic acid complexes seems to concern its more flexible structure.

Keywords: VanadiumIV, *D*-lactobionic acid, stability constants, spectroscopy

INTRODUCTION

Saccharides are very effective chelating agents for many metal ions including vanadyl(IV).[1] The carboxylate group often acts as an anchor binding site but the major role in coordination is played by the deprotonated hydroxyl oxygen atoms. Although sugar acids produce oxovanadium(IV) by reaction with vanadate(V),[2,3] their complexes with vanadyl ions have been rarely investigated.[1,4,5]

Aldobionic acids are often used in medicine[6–9] and agriculture.[10] Their use is attributed to their chelating properties.[6–13] Our recent work on the coordination of lactobionic acid to copper(II) has shown that this ligand binds metal ions very effectively. The complexes formed are more than one hundred times more stable than respective complexes of, *e.g.*, uronic acids, although the binding modes are exactly the same in both ligands.[14]

In this work we present the results of potentiometric and spectroscopic studies on lactobionic acid with vanadyl(IV), an ion which usually forms much stronger complexes with sugar acids than does copper(II).[1]

EXPERIMENTAL

D-Lactobionic acid was obtained from Fluka and used without further purification. Its purity was checked by potentiometry using the Gran method.[15]

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Spectroscopic measurements

EPR spectra were recorded using a Varian E-9 spectrometer at 120 K (X-band, 9.15 GHz). Absorption spectra were recorded on a Uvikon 810P spectrophotometer and CD spectra on a Jobin-Yvon CNRS dichrographe III. Solutions containing 0.002 mol dm^{-3} of metal ion and with a metal to ligand ratio of 1 : 5 were used for spectroscopic measurements.

Potentiometric measurements

Titrations were performed at 25°C with a Tacussel ISIS 2000 pH meter equipped with TB 10/HA glass electrode and a saturated calomel reference electrode. All titrations were carried out under argon and at a constant ionic strength of 0.1 mol dm^{-3} (KNO_3). Carbonate-free 0.1 M NaOH was used as titrant. VO^{2+}-containing solutions were obtained by dissolving $VOSO_4.3H_2O$ in water. Impurities (vanadium(V)) were removed with SO_2. Oxovanadium(IV) chloride was prepared by the addition of barium chloride in stoichiometric amounts. The $VOCl_2$ solutions were standardized with $KMnO_4$. In the solutions containing lactobionic acid the lactone–acid equilibrium alters the real concentration of the acid form. This concentration was evaluated using kinetic parameters obtained earlier.[14] The stability constants were calculated with the SUPERQUAD program[16] which allows for the simultaneous refinement of stability constants together with total ligand and total hydrogen concentrations. The standard deviations quoted were computed by SUPERQUAD and refer to random errors only. These give, however, a good indication of the importance of a particular species in the equilibrium.

TABLE I

Stability constants (logβ) for proton and VO(IV) complexes with *D*-lactobionic acid. Data for VO(IV)-*D*-galacturonic acid and Cu(II)-*D*-lactobionic acid are given for comparison.

Species	lactobionic acid logβ		galacturonic acid[1] logβ
M L H	VO(IV)	Cu(II)[14]	VO(IV)
0 1 0	3.53		3.28
1 2 0	6.07 (0.003)[a]	5.46[b]	
1 2-1	2.32 (0.003)	−0.43	0.47
1 2-2	−1.92 (0.006)	−7.05	−4.01
1 2-3	−10.31 (0.040)	[c]	−12.98
1 2-4	−18.56 (0.130)	−27.06	−22.56

[a] Standard deviations are given in parentheses. [b] This value was obtained from polarographic measurements. [c] This species was not observed with copper(II) ions.

RESULTS AND DISCUSSIONS

It has already been shown that, at acidic pH, lactobionic acid is in equilibrium with the lactone form. Without an anchoring carboxylate, the latter molecule is unable to coordinate metal ions and it should be excluded from the total ligand concentration for calculation purposes. Although the amount of the lactone form is low (8.65% at pH 3.3 and 0.15% at pH 5.6) the equilibrium exchange rate is relatively slow and it influences pH readings considerably. Using results obtained earlier, the real concentration of the acid form was evaluated and used in the calculations. Lactobionic acid has one measurable protonation constant, pK = 3.53, Table I, assigned to the carboxyl function.

TABLE II
Spectroscopic data for the VO(IV)-*D*-lactobionic acid complexes and the assigned donor sets for the respective species.

Species	CD	Absorption	epr		
VO L H	λnm(Δε)	λnm(ε)	g_i	A_i	$\times 10^{-4}$cm^{-1}
1 2 0	730(+0.02)	780(21) 572(7)			A
1 2-1	700(+0.2) 565(−0.01) 530(+0.01)	770(19) 540(15) 395(14)	1.968	96[a]	B
1 2-2	780(−0.01) 640(+0.06) 520(+0.025) 400(+0.03)	760(16) 622(19) 532(20) 392(26)	1.974	81	C
1 2-3	780(−0.02) 610(+0.06) 560(+0.01) 400(+0.03)	782(15) 625(16) 531(16) 407(24)			D
1 2-4	765(−0.27) 737(−0.20) 615(+0.30) 560sh 416(+0.10)	717(24) 720(8) 425(19)	1.975	79[b]	E

[a] The EPR spectra are slightly broad and it is difficult to distinguish between different species with parameters very close to each other. [b] There is only one set of spectra observed between pH 8 and 11 and, although its shape and parameters slightly change, unequivocal assignment is difficult. EPR parameters were not used as basic spectral data for the assignment of the species. They were fitted to the model as judged from CD spectra. A, B, C, D, and E correspond to the following binding modes: 2 × {COO$^-$}, {COO$^-$; COO$^-$, O$^-$}, 2{COO$^-$, O$^-$}, {COO$^-$, O$^-$; 2 × O$^-$} and 2{O$^-$, O$^-$}, respectively, where O$^-$ is a deprotonated hydroxyl group.

Vanadyl(IV) ions form five complex species with lactobionic acid starting at very low pH (<3). No equimolar complexes could be found in the studied solutions, as was the case in the VO(IV)-galacturonic acid system.[1] The coordination modes are the same in both cases and spectroscopic data support the proposed structures (Table II). At very high pH, hydrolysis could be an important process. CD spectra, however, clearly indicate that lactobionic acid is bound to the metal ion even at a pH greater than 11. The distinct increase of Cotton effects with pH between 8 and 11 indicates only the variation of binding sites in lactobionic acid (Fig. 1, Table II). Coordination begins with the carboxyl function which acts as an anchor. When the pH is increased, the metal ion induces the deprotonation of and binds to a vicinal hydroxyl group. The formation of ML_2H_{-3} and MLH_{-4} complexes results from the fact that vanadyl ions are able to induce the deprotonation of two hydroxyls in each ligand molecule. Vanadyl coordination to four deprotonated hydroxyl oxygen atoms is very effective and overcomes the tendency towards metal ion hydrolysis. Although the binding modes of VO(IV) ions with lactobionic acid are the same as with galacturonic acid (the latter ligand was shown to be a very effective chelating agent for vanadyl[1]), the stability constants for lactobionic acid complexes are two to four orders of magnitude higher (Table I). Vanadyl complexes with lactobionic acid are also considerably more stable than the respective copper(II) complexes with the same ligand (Table I).[14] The unusual stability of the lactobionic acid complexes with both metal ions in comparison to uronic acid systems may derive from the fact that the latter ligands, with a cyclic structure, form more rigid chelate rings. Differences in complex stability may thus derive from entropic effects. The importance of the relative position of the hydroxyl group and the chelate ring stability was shown earlier to be an important factor for the stability of metal complexes with aminosugars.[17,18]

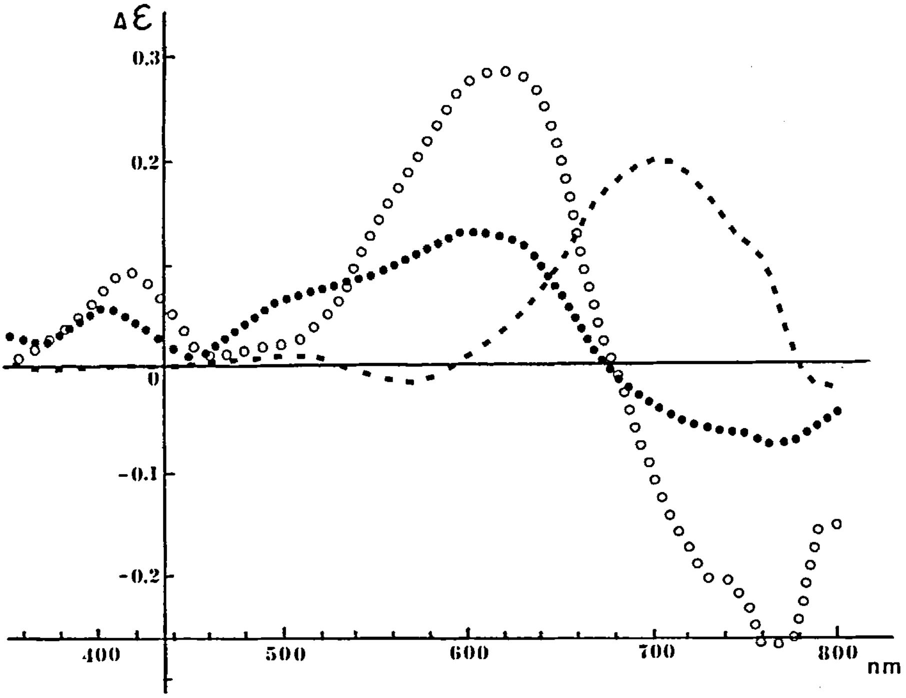

FIGURE 1 Representative CD spectra for VO(IV)-*D*-lactobionic acid solutions with metal concentration 1.96 × 10^{-3} and a 1:5 metal to ligand molar ratio obtained at pH 4.55 (- -), 8.7 (● ●) and 10.6 (O O).

The more flexible structure of the linear fragment of lactobionic acid which coordinates to the metal ion allows the formation of less hindered chelate rings and, as a result, more stable complexes, both in the case of vanadyl(IV) and copper(II) ions. The former ions prefer hydroxyl donors and their complexes are considerably more stable than those of copper(II) (two to eight orders of magnitude, Table I).

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