Studies on Borate Esters. Part 8.[1,2] Interactions of Cations with Oxyacid Anion-bridged Esters of D-Glucarate in Alkaline Media

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Cation co-ordination has been studied in aqueous cation–borate–D-glucarate systems using ^{11}B n.m.r. spectroscopy. The univalent cations K^{I}, Na^{I}, and Ag^{I} do not show preferential co-ordination by the borate esters of D-glucarate. The divalent cations Mg^{II}, Ca^{II}, Co^{II}, Ni^{II}, Sr^{II}, Cd^{II}, and Ba^{II} are co-ordinated by the borate diesters. The cations that ionize the α-hydroxyl functions of D-glucarate, Cu^{II}, Zn^{II}, Pr^{III}, and Pb^{II}, and/or compete with borate for the diol functions, Al^{III} and Fe^{III}, are more strongly co-ordinated by free D-glucarate than by its borate diester. The different behaviour of the cations is discussed in terms of differences in charge/radius density and polarizing ability. In the Ca^{II}–oxyacid anion–D-glucarate system, Ca^{II} ion-selective electrode measurements and Ca^{II} sequestering capacity determinations have been performed. Apart from borate, synergic Ca^{II} co-ordination is observed at high pH for the oxyacid anion esters of D-glucarate of antimonite, stannate, aluminate, and germanate.

Aqueous alkaline solutions of borate and polyhydroxycarboxylates possess good cation sequestering abilities and are applied in the galvanic, glass, and cement industries, and in pharmaceuticals.[3] In addition, these systems have potential as triphosphate substitutes in detergents.[4,5] We have determined the stability and structure of borate mono- and di-esters of a series of polyhydroxycarboxylates (Figure 1) using multinuclear n.m.r. spectroscopy.[6,7] The synergic Ca^{II} co-ordination in these systems finds its origin in the high Ca^{II} co-ordinating strength of the borate diesters of the polyhydroxycarboxylates.[2,8] This effect is most pronounced for D-glucarate (Figure 2) as the polyhydroxycarboxylate.[2,4,5] Formation of the *threo*-3,4-borate diesters of D-glucarate results in the creation of new multidentate Ca^{II} co-ordinating sites.[8] Each of these sites is composed of two carboxylate oxygens, two borate ester ring oxygens, and, depending on the configuration, up to two hydroxyl oxygens (Figure 3).[2,8]

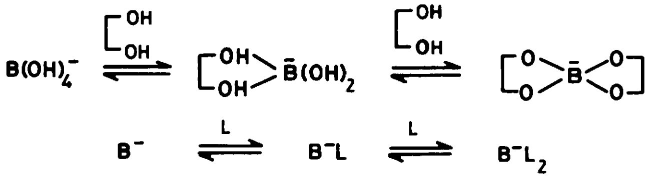

Figure 1. Equilibria between borate (B$^-$) and a diol function of a polyhydroxycarboxylate (L) at pH > 9

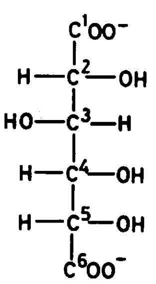

Figure 2. D-Glucarate

Borate (B^{III}) is not unique in forming oxyacid anion esters (or complexes) with diol functions. Other oxyacid anions (X^-) such as aluminate (Al^{III}), silicate (Si^{IV}), germanate (Ge^{IV}), arsenite (As^{III}), selenite (Se^{IV}), stannate (Sn^{IV}), antimonate (Sb^{V}), tellurate (Te^{VI}), and periodiate (I^{VII}) are also capable of doing so.[9–19] It may be noted that synergic Ca^{II} sequestration has been reported for aluminate–D-glucoheptonate (D-glycero-D-guloheptonate) mixtures.[20]

As an extension of our work on borate esters and their Ca^{II} co-ordination,[1,2,6–8] this paper deals with the (synergic) cation co-ordination phenomena in different oxyacid anion–D-glucarate systems. First, the affinity of the cation co-ordination sites in the borate diesters of D-glucarate (Figure 3) at high pH is screened using ^{11}B n.m.r. for a series of cations: M = Na^{I}, Mg^{II}, Al^{III}, K^{I}, Ca^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Sr^{II}, Ag^{I}, Cd^{II}, Ba^{II}, Pr^{III}, and Pb^{II}. Secondly, several oxyacid anion–D-glucarate systems are investigated with respect to their Ca^{II} co-ordinating ability in the pH range 6—12, using Ca^{II} ion-selective electrode (i.s.e.) measurements: B^{III}, Al^{III}, Si^{IV}, Ge^{IV}, As^{III}, As^{V}, Se^{IV}, Sn^{IV}, Sb^{III}, Sb^{V}, Te^{VI}, and I^{VII} are studied as oxyacid anions.

The complexation phenomena in the cation–oxyacid anion–D-glucarate systems are rationalized in terms of differences in the charge/radius density and the polarizing ability of the cations, as quantified with the D values of Marks and Drago given in ref. 21 and the $g_1(z/r^2 + g_2)$ values of Brown *et al.*[22] (z = cationic charge, r = ionic radius, g_1 and g_2 = functions of the electronic structure). In addition, it is demonstrated that the various oxyacid anion–D-glucarate systems obey the 'pH rule of thumb', formulated previously for borate.[23]

Results and Discussion

Cation Addition to the Boric Acid–D-Glucaric Acid System at pH 10.5.—The effects of various cations (0.05 mol dm^{-3}) added to solutions of boric acid (0.1 mol dm^{-3}) and D-glucaric acid (0.1 mol dm^{-3}) in D_2O at pH 10.5 were studied with ^{11}B n.m.r. (Figure 4). In all cases the exchange between borate and the borate monoester and between the borate monoester and the borate diester was slow on the ^{11}B n.m.r. time-scale, whereas the exchange between the borate esters and the corresponding cation complexes was fast.† The changes in ^{11}B chemical shifts upon cation addition were small (< 0.5 p.p.m.).

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† In the presence of Mn^{II} only one broad ^{11}B n.m.r. signal was observed.

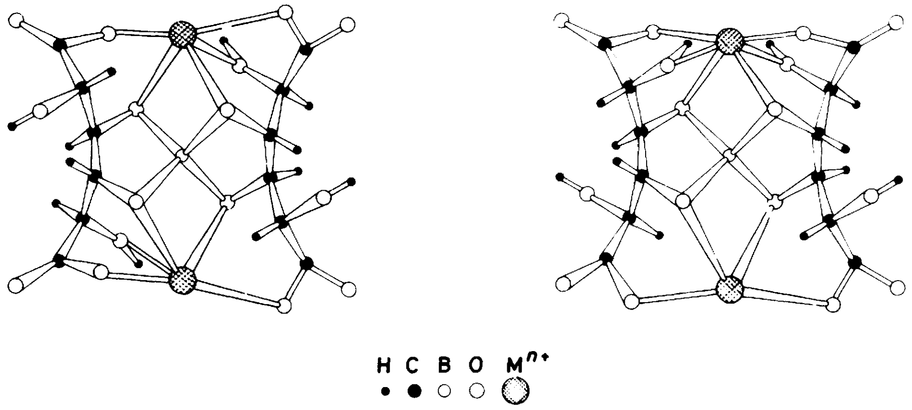

Figure 3. Calcium(II) co-ordination in the diastereomeric (*R*)- and (*S*)-borate diesters of D-glucarate in water

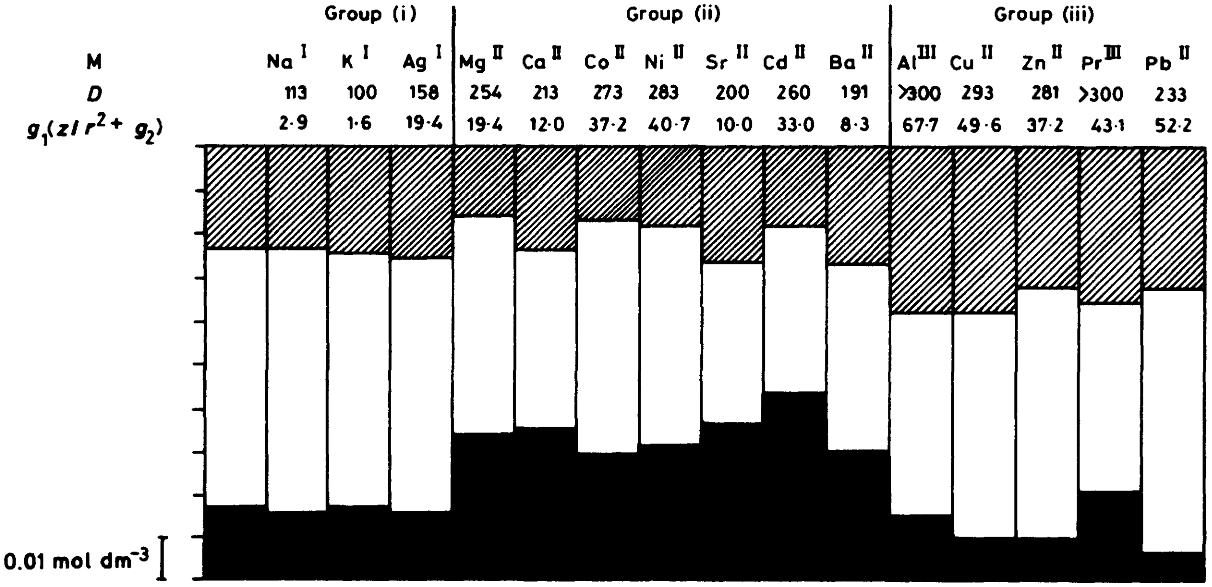

Figure 4. Effect of cations (0.05 mol dm^{-3}) on the distribution of boron-containing species (including corresponding cation complexes) for a solution of boric acid (0.1 mol dm^{-3}) and D-glucaric acid (0.1 mol dm^{-3}) in D_2O at pH 10.5 and 25 °C as determined with ^{11}B n.m.r.: (▨) B^-, (□) B^-L, (■) B^-L_2. For Pr^{III}, [Pr] = 0.01 mol dm^{-3}, pH 8.0, to avoid precipitation and excessive line broadening. Without Pr^{III}, $[B^-]$ = 0.027 mol dm^{-3}, $[B^-L]$ = 0.040 mol dm^{-3}, and $[B^-L_2]$ = 0.033 mol dm^{-3}, respectively. *D* Values are from ref. 21; $g_1(z/r^2 + g_2)$ values are from ref. 22

The cations can be classified into three groups, according to their effect on the borate ester equilibria (Figure 4): (i) hardly any effect, (ii) increase of the borate diester concentration, and (iii) decrease of the borate diester concentration. This distinction between the cations is related to the charge/density and the polarizing ability. One way of quantifying these properties is the equation of Marks and Drago,[21] which relates the acid (A)–base (B) reaction enthalpy (ΔH_{AB}) with terms for electrostatic (*D*) and covalent interactions (*O*): equation (1).

$$-\Delta H_{AB} = [(D_A - D_B)^2 + O_A O_B]^{\frac{1}{2}} \qquad (1)$$

In the case of oxygen-donor atoms only electrostatic interactions are of importance, so that $-\Delta H_{AB}$ is largely determined by the *D* values. Another way of quantifying the effects of the cations are the $g_1(z/r^2 + g_2)$ values of Brown *et al.*,[22] which are calculated measures for electrostatic interactions and polarizing effects: z/r^2 is the charge/radius density, corrected with g_1 and g_2 to obtain an effective charge/radius density. Finally the value of $pK^{ML}_{MH_{-1}L}$* for the equilibrium $ML \rightleftharpoons MH_{-1}L + H^+$ (*cf.* Figure 5) is used as a more practical measure.[24,25]

Group (i) The monovalent cations Na^I, K^I, and Ag^I [$D < 160$, $g_1(z/r^2 + g_2) < 20$, and $pK^{ML}_{MH_{-1}L} > 12$] did not show preferential co-ordination to one of the borate esters or to the free D-glucarate. This is in agreement with the generally observed weak co-ordination of these cations by organic acyclic polyoxygen ligands.[26] However the linewidth of the ^{23}Na signal for a solution of boric acid (0.1 mol dm^{-3}), D-glucaric acid (0.1 mol dm^{-3}), and NaCl (3.0 mol dm^{-3}) at pH 10.0 was *ca.* 30 Hz, which suggests that the average state of the Na^I ions differs from the free hydrated form (8 Hz). Sodium co-ordination does not interfere with the Ca^{II} co-ordination as the linewidth did not change upon Ca^{II} addition.

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* Charges for the cations (M) and polyhydroxycarboxylates (L) are omitted throughout for clarity.

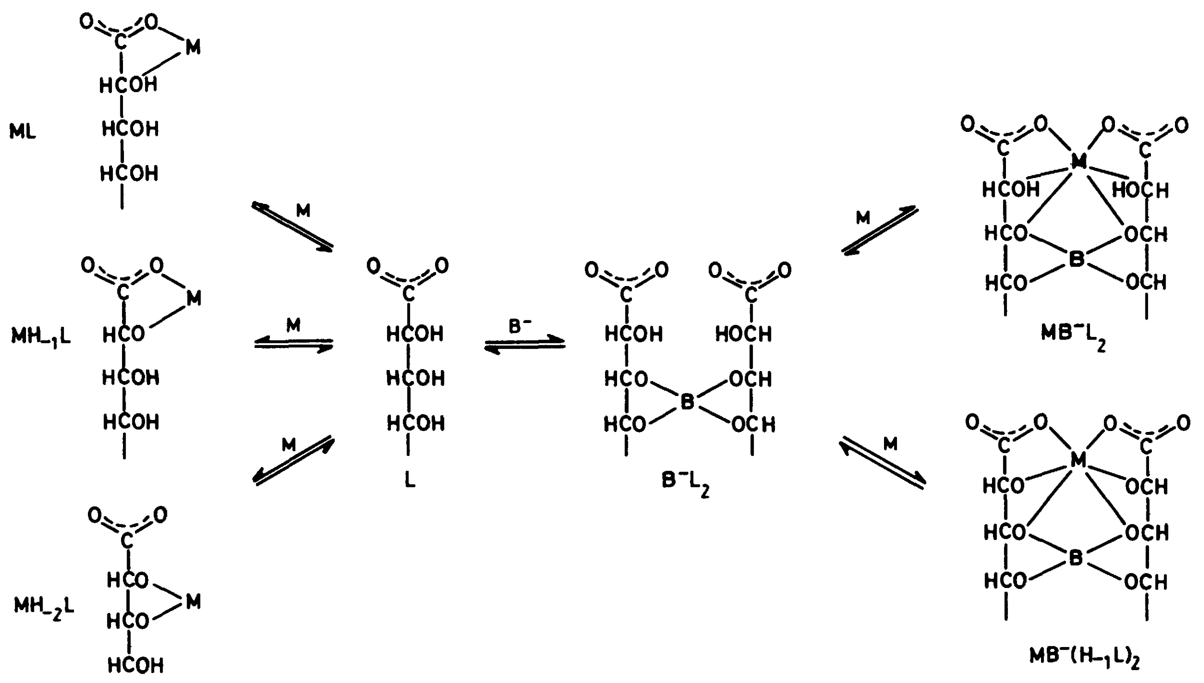

Figure 5. Cation co-ordination in a borate–polyhydroxycarboxylate (B^-–L) system This is a rather schematic representation. The borate monoester and its cation complexes are not included. The co-ordination of M is completed with water molecules and/or hydroxyl groups

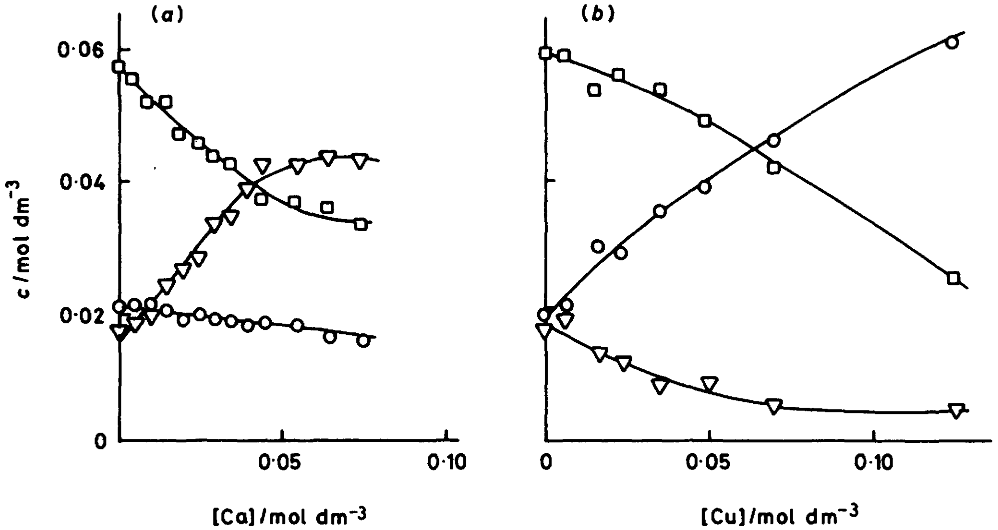

Figure 6. Effect of (*a*) Ca^{II} and (*b*) Cu^{II} on the distribution of boron-containing species (including corresponding cation complexes) for a solution of boric acid (0.1 mol dm^{-3}) and D-glucaric acid (0.1 mol dm^{-3}) in D_2O at pH 10.5 and 25 °C as determined with ^{11}B n.m.r.: (○) B^-, (□) B^-L, (▽) B^-L_2

Group (ii). In the presence of divalent cations with moderate polarizing abilities, Mg^{II}, Ca^{II}, Co^{II}, Ni^{II}, Sr^{II}, Cd^{II}, and Ba^{II} [$190 < D < 280$, $10 < g_1(z/r^2 + g_1) < 40$, and $8 < \mathrm{p}K^{\mathrm{ML}}_{\mathrm{MH_{-1}L}} < 12$], the amount of borate diester-containing species of D-glucarate (esters and their cation complexes) increased and all ^{11}B n.m.r. signals were broadened. These results demonstrate that the co-ordinating strengths of the borate diesters for these cations are of the same order of magnitude as for Ca^{II}.[8,*] As the ionic radii of the cations of group (ii) vary from 0.7 to 1.7 Å,[27] these data indicate that the cation-co-ordinating sites of the borate diesters of D-glucarate are rather flexible. This can be understood by the rotational freedom around C(1)–C(2)/C(6)–C(5) and C(2)–C(3)/C(5)–C(4) bonds, and the flexibility of the five-membered borate ester rings.[28]

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[*] Copper(II), nickel(II), and cadmium(II) co-ordination was investigated in more detail. Addition of Co^{II} and Ni^{II} to a solution of boric acid (0.1 mol dm^{-3}) and D-glucaric acid (0.1 mol dm^{-3}) in D_2O at pH 10.5 resulted in excessive line broadening in the ^{1}H n.m.r. spectra. For Cd^{II} this phenomenon was less obstructive, but induced shifts were small (<0.05 p.p.m. at $c_{Cd} = 0.1$ mol dm^{-3}) and the vicinal ^{1}H coupling constants did not change. Cobalt(II)-induced shifts were measured for the carboxylate signal in ^{17}O n.m.r. spectra of a solution with D-glucaric acid (5% ^{17}O-enriched carboxylic acid groups; 0.1 mol dm^{-3}) in D_2O at pH 10.5 and 66 °C. The induced shifts were larger in the presence of boric acid (0.1 mol dm^{-3}).

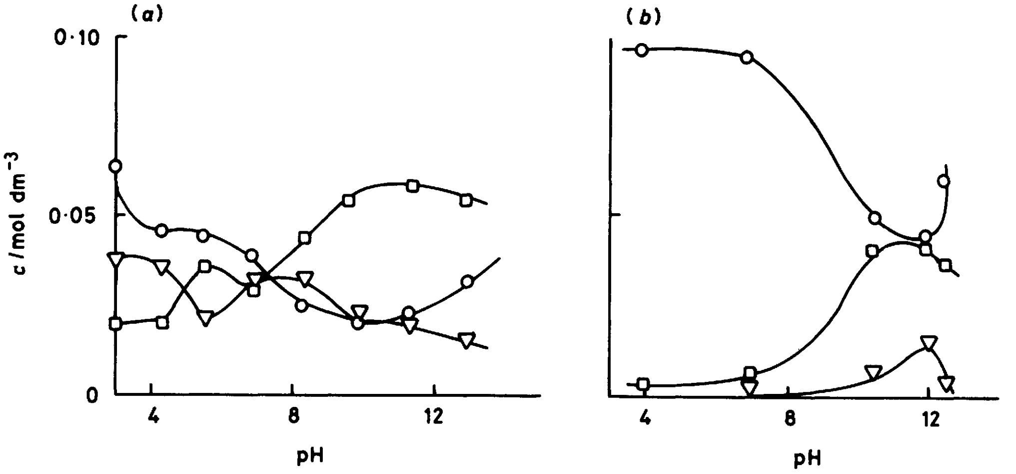

Figure 7. Distribution of boron-containing species (including corresponding cation complexes) for a solution of boric acid (0.1 mol dm^{-3}) and D-glucaric acid (0.1 mol dm^{-3}) in D_2O in the absence (*a*) and presence (*b*) of Al^{III} (0.1 mol dm^{-3}) as a function of the pH at 25 °C as determined with ^{11}B n.m.r.: (○) $B^0 + B^-$, (□) B^-L, (▽) B^-L_2; B^0 = boric acid

Table 1. Effect of [OH$^-$] on the concentration (mol dm^{-3}) of boron-containing species (c_B = 0.1 mol dm^{-3}) for D-mannitol (0.1 mol dm^{-3}) and D-glucaric acid (0.2 mol dm^{-3}) in D_2O at 25 °C as determined with ^{11}B n.m.r.

Polyhydroxy compound	Species*	[OH$^-$] = 0.01	[OH$^-$] = 0.5
D-Mannitol	B^-	0.012	0.046
	B^-L	0.057	0.054
	B^-L_2	0.031	0.000
D-Glucaric acid	B^-	0.002	0.030
	B^-L	0.013	0.070
	B^-L_2	0.085	0.000

* For symbols see Figure 1.

Group (iii). The polyvalent and strongly polarizing cations, Al^{III}, Cu^{II}, Zn^{II}, Pr^{III}, and Pb^{II} [$D > 280, g_1(z/r^2 + g_2) > 40$, and p$K^{ML}_{MH_{-1}L} < 8$] † induced dissociation of the borate esters. A comparison of stepwise Ca^{II} and Cu^{II} addition to the borate–D-glucarate system (Figure 6) demonstrates the different behaviour of cations of groups (ii) and (iii). Ionization of α-hydroxyl functions upon cation co-ordination and/or borate substitution is responsible for these phenomena, as will be explained below.

The acidity of an acid function increases upon co-ordination to a cation; the potentiometric determination of the stability constant of a metal complex is actually based on this principle.[29] The enhancement of the acidity of an α-hydroxyl group upon cation co-ordination increases with higher charge/radius density of the cation. That is, increase of the D and $g_1(z/r^2 + g_2)$ values results in a decrease in p$K^{ML}_{MH_{-1}L}$. In the presence of cations of group (iii), the α-hydroxyl groups of D-glucarate are ionized at pH 10.5.

The essential equilibria of a cation–borate–polyhydroxy-carboxylate (M–B$^-$–L) system are shown in Figure 5. For cations of group (ii) the stability of MB^-L_2 is greater than that of ML and ML_2, as shown above. This is in contrast to cations of group (iii), for which the species $MH_{-1}L$ and $M(H_{-1}L)_2$ have a greater stability than $MB^-(H_{-1}L)_2$. Several factors may influence the stability of the species involved. First, the stability of borate esters of polyols with ionized hydroxyls adjacent to the borate ester ring is relatively low, due to electrostatic repulsion and the absence of possible stabilizing hydrogen bonds[6,30–33] between ionized hydroxyls and the BO_4 moiety. In the absence of multivalent cations this phenomenon was only observed at pH > 13 (Table 1). Secondly, the stability of $M(H_{-1}L)_n$ is relatively high, as a result of the deprotonated α-hydroxyl groups. Thirdly, the behaviour of some cations of group (iii) can be explained by competition with borate for the diol functions. In particular, this will be the case for cations of group (iii) with high $g_1(z/r^2 + g_2)$ values (> 60), such as Al^{III}, where all co-ordinated water molecules are ionized under the present conditions. Oxyacid anions are formed, resulting in oxyacid anion esters [Figure 5, $M(H_{-2}L)_n$], comparable with borate esters.[34]

Competition between Al^{III} and B^{III} for the co-ordinating sites of D-glucaric acid was studied as a function of the pH using ^{11}B n.m.r. (Figure 7). At pH < 8 both Al^{III} and B^{III} prefer co-ordination by the α-hydroxycarboxylate functions of D-glucarate. Obviously, the $M(H_{-1}L)_n$ complexes of Al^{III} are more stable than those of B^{III}. Since the $g_1(z/r^2 + g_2)$ value of B^{III} is larger than that of Al^{III}, B^{III} occupies the diol functions at 8 < pH < 11, at which Al^{III} remains at the α-hydroxycarboxylic acid functions. As a result, mixed binuclear complexes are probably formed. The stability of the borate esters is affected by Al^{III} at pH > 11, when aluminate esters of the diol functions are formed also.

Similar effects are expected for Fe^{III}, also of group (iii), with $g_1(z/r^2 + g_2) = 91$.[22] It explains, for instance, the observation that increase of pH (>1% NaOH) decreases the synergic Fe^{III} sequestration of 'borogluconate', a commercially available Fe^{III} sequestering agent which is a mixture of borate and gluconate. At high pH (>4% NaOH) the Fe^{III} sequestering capacity of borogluconate equals that of D-gluconate.

Calcium(II) *Co-ordination in Oxyacid Anion–*D*-Glucarate Systems.*—The concentration of free hydrated Ca^{II} was determined in solutions of Ca^{II} (5 mmol dm^{-3}) and the oxyacid (5 mmol dm^{-3}) in the absence and presence of D-glucaric acid (10 mmol dm^{-3}) at I = 0.1 mol dm^{-3} and 25 °C as a function of the pH using a Ca^{II} i.s.e. [Figure 8(*a*) and (*b*), respectively]. The Ca^{II} i.s.e. was poisoned when I^{VII} (only in the absence of D-

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† For Pb^{II} the $g_1(z/r^2 + g_2)$ and p$K^{ML}_{MH_{-1}L}$ values fall in the indicated regions; this is not so for the D value, which is probably too low. From an extrapolation of the data from ref. 21, it follows that the D values for trivalent cations are probably larger than 300.

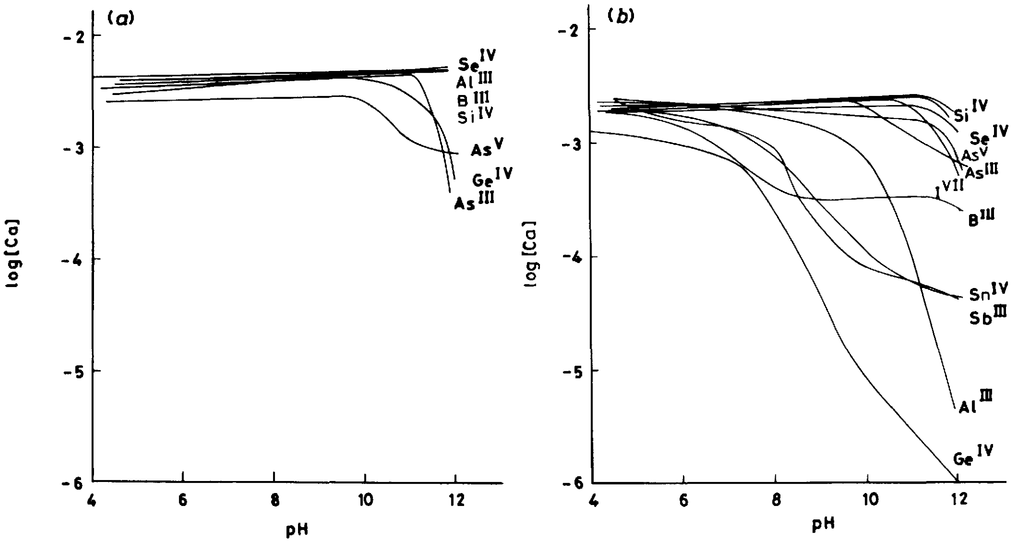

Figure 8. Influence of the pH on log [Ca] (mol dm^{-3}) for a solution of Ca^{II} (5 mmol dm^{-3}) and an oxyacid (5 mmol dm^{-3}) in the absence (*a*) and presence (*b*) of D-glucaric acid (10 mmol dm^{-3}) at $I = 0.1$ mol dm^{-3} and 25 °C as measured with a Ca^{II} i.s.e.

glucaric acid) and Sb^{V} were tested. For Te^{VI} precipitation of $CaTeO_4$ was responsible for the low [Ca], both with and without D-glucaric acid.* All the other oxyacid (anions) as such showed only a moderate Ca^{II} binding capacity, typically log [Ca] > -3.

The mixed-ligand systems demonstrated synergic Ca^{II} co-ordination in the case of B^{III}, Sn^{IV}, Sb^{III}, Al^{III}, and Ge^{IV} oxyacid anions, whereas synergic effects were negligible for Si^{IV}, Se^{IV}, As^{III}, and As^{V} (Figure 8). These phenomena will be discussed on the basis of the model previously derived for B^{III}.[2,8] At pH > 6, boric acid reacts with D-glucarate with formation of borate esters. The borate diesters of D-glucarate have a high Ca^{II}-co-ordinating strength and as a result [Ca] decreases. At pH > 9, boric acid is completely converted into borate and, therefore, both borate ester formation and the Ca^{II} co-ordination equilibria are now unaffected by the pH.

For Al^{III}, As^{III}, and Sb^{III} oxyacid anions comparable to borate [$B(OH)_4^-$] are formed, *viz.* aluminate [$Al(OH)_4^-$; pH > 11], arsenite [$As(OH)_4^-$; pH > 9], and antimonite [$Sb(OH)_4^-$; pH > 11].[24,25,35] These oxyacid anions will form the corresponding esters of D-glucarate. The overall association constant ($\beta_{X^-L_2}$) for the aluminate diesters (X^-) of polyhydroxycarboxylates is *ca.* 10^5 times that of the borate diesters,[6,11] whereas the value for As^{III} is only 10^{-2} to 10^{-3} times that for B^{III}.[6,14,24,25] These differences in $\beta_{X^-L_2}$ explain the differences in [Ca] observed for B^{III}, Al^{III}, and As^{III} [Figure 8(*b*)], when it is assumed that the Ca^{II} co-ordination of the oxyacid anion diesters of D-glucarate is of comparable strength. If this is the case, $\beta_{X^-L_2}$ for Sb^{III} (X^- = antimonite) is 10^2 times that of B^{III} [X = borate (B^-)].

Silicate [$SiO_n(OH)_{4-n}{}^{n-}$; at pH > 10, $n > 1$][24,25] contains at most three hydroxyl groups and, consequently, only silicate monoesters of D-glucarate are formed at higher pH.[16] Arsenate [$H_nAsO_4{}^{(n-3)-}$; pH > 7, $n < 2$] and selenite (SeO_3^{2-}; pH > 8) do not possess more than one hydroxyl function,[24,25] and, therefore, show no oxyacid anion ester formation. As oxyacid anion diesters of D-glucarate are the Ca^{II}-co-ordinating species, this explains why no synergic Ca^{II} co-ordination is observed for Si^{IV}, As^{V}, and Se^{IV}.

Finally, germanate [$Ge(H_2O)_{6-n}(OH)_n{}^{(n-4)-}$; $n > 4$] and stannate [$Sn(OH)_6^{2-}$] are the predominant species for Ge^{IV} and Sn^{IV} at pH > 9 and pH > 11, respectively.[24,25] With D-glucarate these sexidentate oxyacid anions may form either triesters, which possibly results in increased co-operation between three D-glucarates with respect to the Ca^{II} co-ordination, or diesters with possible co-operative co-ordination of two oxyacid anion hydroxyl functions with two D-glucarates.

For oxyacid anions exhibiting synergic Ca^{II} co-ordination in the presence of D-glucarate [X^- = borate(III), aluminate(III), germanate(IV), antimonite(III), and stannate(IV)], [Ca] was measured at pH 10.0—11.5, $I = 0.1$ mol dm^{-3}, and 25 °C as a function of the molar fraction of D-glucarate (x_g): equation (2).

$$x_g = c_g/(c_X + c_g) \qquad (2)$$

The results for B^{III}, Al^{III}, and Ge^{IV} again demonstrated the synergic Ca^{II} co-ordination (Figure 9). The curve for Ge^{IV} was influenced by kinetic effects because of the very low rates of germanate ester formation,[14] while precipitation occurred at $x_g < 0.2$. For Sn^{IV} and Sb^{III} clear solutions were only obtained in the presence of a substantial amount of D-glucarate.

Calcium(II) sequestering capacities (s.c.s) were measured using a titration procedure with oxalate as the indicator in order to obtain more practical data for synergic Ca^{II} co-ordination and to check whether, for the Al^{III} and Ge^{IV} systems, [Ca] is extremely low. Barium(II) s.c.s, determined with sulphate as indicator, were included because sequestration of Ba^{II} is of relevance in oil exploitation and our ^{11}B n.m.r. data indicate that the oxyacid anion–D-glucarate mixed-ligand systems might be of importance in that area. The data in Table 2 demonstrate that addition of oxyacid anions to a D-glucarate solution had a large effect on both Ca^{II} and Ba^{II} sequestration, in particular at pH 12.5. The effects of the oxyacid anions upon the metal s.c.s seem less spectacular than with the Ca^{II} i.s.e. measurements, since a decrease in [Ca] from 0.1 to 0.01 mmol dm^{-3} only amounts to an increase in co-ordinated Ca^{II} from 4.9 to 4.99 mmol dm^{-3}. The metal s.c.s correspond with cation:D-glucarate ratios of 0.5—1.0:1, which supports the existence of dication(II) complexes. For Al^{III} this ratio is >1:1, which indicates that other Ca^{II} complexes are predominant.

It has been mentioned briefly that the difference between cations and oxyacid anions becomes rather vague for Al^{III} and

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* From [Ca] as a function of the pH in the absence of D-glucaric acid, the solubility product of $CaTeO_4$ was calculated to be 2×10^{-8} mol^2 dm^{-6}.

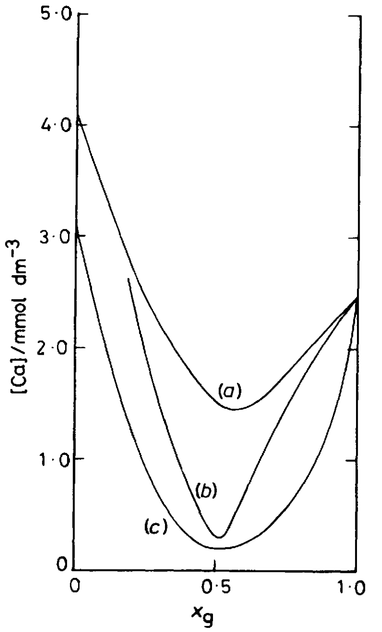

Figure 9. Free $\mathrm{Ca^{II}}$ concentration as a function of the molar fraction of D-glucaric acid (x_g) for various $\mathrm{Ca^{II}}$–oxyacid anion–D-glucaric acid systems ($c_X + c_g = 10$ mmol dm^{-3}, $c_{Ca} = 5$ mmol dm^{-3}, $I = 0.1$ mol dm^{-3}, and 25 °C) as measured with a $\mathrm{Ca^{II}}$ i.s.e.: (*a*) $\mathrm{B^{III}}$, pH 10.0; (*b*) $\mathrm{Ge^{IV}}$, pH 11.0; (*c*) $\mathrm{Al^{III}}$, pH 11.5

Table 2. Calcium(II) and barium(II) sequestering capacities (g of metal ion per 100 g D-glucaric acid) in oxyacid anion–D-glucaric acid systems at high pH and 25 °C

Oxyacid anion	mol oxyacid anion / mol D-glucaric acid	pH	$\mathrm{Ca^{II}}$ s.c.	$\mathrm{Ba^{II}}$ s.c.
Borate(III)	0.5	11.0	10.9	38.7
	0.5	12.5	15.9	
Aluminate(III)	0.5	11.0	14.7	31.2
	0.25	12.5	21.3	
	0.5	12.5	23.0	39.8
Borate(III) + aluminate(III)	0.25 + 0.25	12.5	27.8	
	0.5 + 0.5	12.5	26.0	
Germanate(IV)	0.5	11.0		43.0
Antimonite(III)	0.5	11.0	11.6	33.6
Stannate(IV)	0.5	11.0	14.5	34.9

$\mathrm{Fe^{III}}$. A general co-ordination–ionization scheme for cation–oxyacid anion–polyhydroxycarboxylate systems will be presented in a forthcoming paper.[34]

Experimental

Hydrogen-1, ^{11}B, ^{17}O, and ^{23}Na n.m.r. spectra were recorded with a Nicolet NT-200 WB spectrometer at 200.07, 64.19, 27.12, and 52.92 MHz, respectively, at 25 °C. The samples contained a polyhydroxycarboxylic acid (0—0.2 mol dm^{-3}), boric acid (0—0.15 mol dm^{-3}), and a metal salt (0—0.3 mol dm^{-3}) in D_2O at pH > 9 (unless stated otherwise).

Free $\mathrm{Ca^{II}}$ concentrations were determined with a Philips IS 561-Ca i.s.e., a HNU ISE-40-01-100 single-junction reference electrode, and a Corning digital 112 pH meter. The $\mathrm{Ca^{II}}$ i.s.e. was calibrated as a function of the pH and a linear drift correction was applied. The aqueous solutions of calcium(II) chloride (5 mmol dm^{-3}), D-glucaric acid (0—10 mmol dm^{-3}), and an oxyacid (0—10 mmol dm^{-3}) at $I = 0.1$ mol dm^{-3} (KCl) were flushed with nitrogen. The measurements were performed at 25 °C under a nitrogen atomosphere. The pH was adjusted with NaOH.

Calcium(II) s.c.s were determined according to Wilham and Mehltretter,[36] using a titration procedure with oxalate as indicator at pH 11.0 or 12.5 (NaOH). Barium(II) s.c.s were determined in a similar way with sulphate as indicator. Oxalate was tested as indicator, but the solutions turned turbid slowly and the $\mathrm{Ba^{II}}$ s.c. of a solution without any sequestering agent was 2 g $\mathrm{Ba^{II}}$ per 25 cm^3.

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