747. *The Chemistry of Quadrivalent Germanium. Part VIII.* Complexes of Germanium with Tartaric, Lactic, and Mucic Acid.*

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The complexes formed between germanic acid and tartrate, lactate, and mucate have been studied by ion-exchange methods. With tartaric acid the 1 : 1 tartrate–germanium complex has been confirmed as occurring at low tartrate (= Ta) concentrations, above which the 3 : 2 complex occurs. Evidence has been obtained that polynuclear species of the type $Ge_xTa_{x-1}{}^{x-}$, where x is *ca.* 5, exist in solutions containing much germanium and tartrate. With lactic acid evidence has been obtained for the occurrence of 3 : 1, 2 : 1, and 1 : 1 lactate–germanium complexes. The mucic acid complexes of germanium appear to resemble those of lactic acid at low pH, tartaric acid complexes at middle pH, and polyhydric alcohol complexes at high pH values. Tentative suggestions are made concerning the structure of the complexes.

Compounds with two adjacent hydroxyl or carboxyl groups have been shown to form stable complexes with germanium.[1,2] Complexes from compounds containing only carboxyl groups are most stable below pH 7 and break down in alkaline solution, whereas those from di- and poly-hydroxy-compounds are most stable at high pH values and relatively unstable in acidic media. Compounds possessing adjacent hydroxyl and carboxyl groups would be expected to show complex-forming behaviour intermediate between those of the first two ligand classes.

Hydroxy-acids may be divided into two categories, simple hydroxy-acids containing the minimum number of groups required to afford a complex with germanium, *e.g.*, lactic acid, and compounds containing more than this minimum number of groups, such as tartaric and mucic acid. Complexes formed by acids of each group with germanium have

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* Part VII, *J.*, 1960, 1745.

[1] Everest, *J.*, 1955, 4415.

[2] Everest and Harrison, *J.*, 1957, 4319.

been recently described. Vartapetian *et al.*[3,4] concluded from conductivity, pH, and optical-activity measurements that tartaric acid forms only a 1 : 1 ligand–germanium complex; this complex is stable below pH 6 but decomposes at pH 6—10. It was also reported that lactic and mandelic acid formed respectively 2 : 1 and 3 : 1 ligand–germanium complexes. Mattock[5] found strong evidence for the 1 : 1 tartrate–germanium complex, and also put forward evidence for the existence of 2 : 1 and 1 : 2 tartrate–germanium complexes. Pflugmacher and Rohrman[6] also found evidence for the 1 : 1 tartrate–germanium complex but disagreed with Vartapetian's findings[4] concerning mandelic acid which they reported as forming a 2 : 1 ligand–germanium complex, which they isolated as neutral crystals.

Clark and Waddams[7] and Clark[8] have made a brief survey of the complexes formed between germanium and twenty-four hydroxy-acids and have suggested combining ratios under the conditions used; in three cases, mandelic, benzilic, and hydroxyhexanoic acid, neutral 2 : 1 ligand–germanium complexes were isolated in crystalline form.

As in previous investigations in this series, we used ion-exchange methods. In this instance they possess the advantages of being different from the techniques used in previous investigations and of allowing study of more concentrated solutions.

EXPERIMENTAL

Solutions.—These were prepared in a manner analogous to that previously described.[9] Lactic acid solutions were boiled immediately before use to decompose any lactide or lactyl-lactic acid present.[4] pH values were adjusted by addition of sodium hydroxide or hydrochloric acid.

Resins.—Amberlite I.R.A.400 in the chloride, tartrate, lactate, or mucate form was used in most experiments; details of the preparation of these resin salt forms are given elsewhere.[10] Solutions were equilibrated for at least 14 days with regular shaking.

Analytical Methods.—Germanium and chloride were determined, respectively, iodometrically[11] and gravimetrically as silver chloride. Tartrate, lactate, and mucate were determined iodometrically as described elsewhere.[10]

R *Values and Controls for Various Systems.*—*R* values (moles of acid occupying one equivalent of resin [12,13]) for tartaric, lactic, and mucic acid are included in the Tables of results for the systems studied. The *R* values for lactic acid rise above one at low pH values owing to sorption of lactyl-lactic acid, the formation of the latter being apparently catalysed by the resin as the solution was freed from condensation products of lactic acid by prior boiling. In order to minimise the importance of the *R* value of free lactic acid in calculation, all experiments in the germanium–lactic acid system were so devised that the resin was largely satisfied by complex or complex plus chloride.

In systems containing high concentrations of organic acids at low pH values a high proportion of the acid is un-ionised and invades the resin as non-exchange electrolyte; this has been allowed for by control experiments. In determining such control values, and in all actual experiments, it is essential to standardise rigidly the washing procedure and to use a relatively large resin bead-size (20—30 mesh) to facilitate rapid washing.

RESULTS AND DISCUSSION

Germanium–Tartaric Acid System.—Section a of Table 1 contains results of experiments with 26 mg.-atoms of germanium and 75 mmoles of tartrate per l. Between pH 0·78

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[3] Vartapetian and Tchakarian, *Compt. rend.*, 1953, **236**, 81.
[4] Vartapetian, *Ann. Chim.* (*France*), 1957, **2**, 916.
[5] Mattock, *J.*, 1954, 989.
[6] Pflugmacher and Rohrman, *Angew. Chem.*, 1957, **69**, 78.
[7] Clark and Waddams, *Nature*, 1957, **180**, 904.
[8] Clark, *Nature*, 1959, **183**, 536.
[9] Everest and Harrison, *J.*, 1960, 1745.
[10] Harrison, Thesis, London, 1959.
[11] Everest, *J.*, 1953, 4117.
[12] Everest and Salmon, *J.*, 1954, 2438; Everest and Harrison, *J.*, 1959, 2178
[13] Russell and Salmon, *J.*, 1958, 4708.

and pH 9 the resin capacity can be accounted for in terms of sorption of a univalent 1 : 1 tartrate–germanium complex together with free tartrate. Below pH 1·24 the presence of hydrochloric acid inhibits the sorption of free tartrate, so that resin sites not occupied by complex are occupied by chloride. Above pH 11 the 1 : 1 complex is completely dissociated, the resin capacity being accounted for in terms of sorption of free germanate and tartrate. In the pH range 9—11 a mixture of germanate, tartrate, and 1 : 1 complex is sorbed by the resin. This picture of a predominant 1 : 1 complex in dilute solution of germanium and tartrate agrees with the conclusions reached by previous workers.[3-5] The breakdown of the complex in the pH range 9—11 agrees approximately with Vartapetian's conclusions.[4]

TABLE 1. *Sorption of germanium and tartrate from solutions by Amberlite* I.R.A. 400-Ta.

Section a. Germanium and tartrate concns. 26 mg.-atoms and 75 mmoles per l. respectively. Solution 150 ml.; 0·5 g. of resin.

	Species sorbed; mole or g.-atom per equiv. of resin			*R* value of free Ta	Resin capacity, equiv. per equiv. of resin, calculated for	
pH	Ge	Ta	Cl		$GeTa^-$ + Ta	Germanate + Ta
0·78	0·71	0·725	0·265	1·0	0·99	—
1·2	0·865	0·87	0·085	1·0	0·96	—
1·8 *	0·885	0·825	—	0·75	—	—
2·9	0·715	0·865	—	0·5	1·01	—
4·5	0·67	0·82	—	,,	0·97	—
6·05	0·60	0·805	—	,,	1·01	—
7·6	0·58	0·81	—	,,	1·04	—
8·15	0·57	0·79	—	,,	1·03	—
8·95	0·50	0·74	—	,,	0·99	2·48
10·2	0·34	0·50	—	,,	0·66	1·68
11·1	0·135	0·44	—	,,	0·80	0·98
12·0	0·115	0·41	—	,,	0·77	0·97

Section b. 3 mg.-atoms of germanium, 3—450 mmoles of tartrate. Solution 75—100 ml.

		Species sorbed; mole or g.-atom per equiv. of resin				Resin capacity, equiv. per equiv. of resin, calculated for	
mmoles of Ta in soln.	pH *	Ge	Ta	Non-exchange Ta	*R* value of free Ta	$GeTa^-$ + Ta	$Ge_2Ta_3^{2-}$ + Ta
6	1·45	0·78	1·00	—	0·90	1·02	—
9	1·40	0·74	0·995	—	1·00	0·995	—
12	1·36	0·73	1·03	—	,,	1·03	—
15	1·32	0·70	1·07	—	,,	1·07	—
18	1·30	0·685	1·10	—	,,	1·10	0·76
24	1·26	0·675	1·20	—	,,	1·20	0·83
30	1·18	0·595	1·32	—	,,	1·32	1·00
45	1·14	0·57	1·32	0·05	,,	1·32	1·03
120	1·06	0·50	1·31	0·25	,,	—	1·06
240	0·96	0·40	1·23	0·45	,,	—	1·03
300	0·68	0·38	1·24	0·57	,,	—	1·05
450	0·52	0·23	1·19	0·70	,,	—	1·07

* The natural pH of the system.

There is one discrepant result in section a of Table 1 at the natural pH of the system (1·8) where the capacity of the resin cannot be accounted for in terms of the sorption of a 1 : 1 complex plus free tartrate. As it is most unlikely that any free germanate is sorbed by the resin at this particular pH, it appears that some of the complex ions entering the resin phase contain relatively more germanium than do the simple 1 : 1 complexes. This by atypical behaviour at the natural pH is due to lack of effective competition for the resin sites caused by the low degree of ionisation of the system at this pH. This leads to appreciable sorption of ions that are only minor constituents of the system; this effect can often be of use in detection of such minor species.

Section b of Table 1 gives results of experiments with solutions containing 30—40 mg.-atoms of germanium per l. and increasing amounts of tartaric acid at the natural pH, the highest solution mole ratio being 150 : 1. The result with equal quantities of tartrate and germanium resembles the result at pH 1·8 in section a, in that a small amount of complex with a tartrate : germanium ratio of less than unity is sorbed together with the 1 : 1 complex. Between tartrate : germanium solution mole ratios of 2 : 1 and 5 : 1 the resin capacity can be accounted for solely in terms of sorption of the 1 : 1 complex plus free tartrate. Between solution ratios of 15 : 1 and 100 : 1 the resin capacity is accounted for in terms of sorption of a doubly charged 3 : 2 tartrate : germanium complex plus free tartrate. At higher tartrate : germanium solution ratios some singly charged 3 : 2 complex is taken up by the resin.

Some indication as to the nature of the complexes with tartrate : germanium ratios less than unity has been obtained by experiments with solutions containing 20—280 mg.-atoms of germanium per l. and with a 1 : 2 tartrate : germanium solution ratio at the natural pH of the system (here and elsewhere more detailed results are given in ref. 10). As it is unlikely that any free germanate or tartrate will be sorbed by the resin at these low pH values (1·6—1·1), and as it can be assumed that in presence of excess of germanium no free tartrate will be sorbed by the resin, the ratio of tartrate : germanium on the resin approximates to the mean tartrate : germanium ratio in the sorbed complexes. It was found that at germanium solution concentrations of at least 80 mg.-atoms per l. the tartrate : germanium resin ratio was *ca.* 0·8 and the total amount of germanium sorbed was *ca.* 1·0—1·1 equiv. per equiv. of resin. Such results would accord with the sorption by the resin of germanium-rich polynuclear species such as $Ge_5Ta_4^{x-}$ where $x = 4$—5.

Repeating these experiments but with a 2 : 1 tartrate : germanium solution ratio gave very similar results, except at the highest concentrations (>330 mmoles of tartrate per l.), indicating that germanium-rich polymers were still sorbed by the resin despite the excess of tartrate in solution. At tartrate concentrations above 330 mmoles per l. these germanium-rich polynuclear species appear to be broken down, and only the 1 : 1 tartrate–germanium complex is taken up by the resin. Thus the highest tartrate-rich species appears to be the 3 : 2 complex which is sorbed by the resin from solutions containing a 10 : 1 or greater tartrate–germanium ratio (section b, Table 1).

Germanium–Lactic Acid System.—In sections a and b of Table 2 are given results for solutions containing 30 and 40 mg.-atoms of germanium and 90 and 400 mmoles of lactic acid respectively. Except at the lower pH values, where the 3 : 1 lactate–germanium complex appears to be the chief complex species sorbed, the resin capacity below pH 8 cannot be accounted for in terms of sorption of any one complex plus free lactate. $GeLa_3^{2-}$ or $GeLa_2^{-}$ gives low calculated capacities, whilst $GeLa_2^{2-}$ or $GeLa^{-}$ gives calculated capacities which are too high. It seems probable that a mixture of all these complexes is being sorbed by the resin, the proportion of the 1 : 1 species sorbed increasing with increased pH. Above pH 8 the complexes break down into free germanate and lactate, and the capacity can be quantitatively accounted for in terms of sorption of these two species. As was also found in the tartrate system the results obtained at the natural pH of the lactate systems are anomalous.

In section c of Table 2 are shown results obtained from solutions containing greater quantities of germanium and lactate in presence of hydrochloric acid. At these acidities sorption of lactate ion is negligible, but allowance must be made for invasion of the resin by non-exchange lactic acid. These results indicate that the 3 : 1 lactate–germanium complex is the only species capable of competing with chloride. The resin capacity cannot be accounted for in terms of sorption of either $GeLa_3^{-}$ or $GeLa_3^{2-}$ alone, and it appears that a mixture of these two species is sorbed under these conditions, the average charge on the complex being *ca.* 1·5.

Germanium–Mucic Acid System.—Mucic acid, with two carboxyl groups separated by four CH(OH) groups, could conceivably react with germanic acid in three different ways. With six potential ligand groups it could form a strong 1 : 1 complex similar to the 1 : 1 tartrate–germanium complex; or each carboxyl with its adjacent hydroxyl groups could behave as an independent co-ordinating centre so that mucic acid would behave as a dilactic acid; or mucic acid could react only through its hydroxyl groups, so resembling mannitol in its complex-forming reactions.

The investigation of this system is severely hampered by the low solubility of mucic

TABLE 2. *Sorption of germanium and lactate from solutions by Amberlite* I.R.A. 400-La.

Section a. Germanium and lactate concns. 30 mg.-atoms and 90 mmoles per l. respectively. Solution 75 ml.; 0·5 g. of resin.

	Species sorbed; mole or g.-atom per equiv. of resin			*R* value of free	Resin capacity, equiv. per equiv. of resin, calculated for			
pH	Ge	La	Cl	La	$GeLa_3^{2-}$ + La	$GeLa_2^-$ + La	$GeLa^-$ + La	Germanate + La
1·15	0·05	0·15	0·995		1·06	—	—	—
1·75 *	0·50	1·275	—	1·7	—	0·62	0·96	—
3·15	0·47	1·54	—	1·4	1·03	0·82	1·22	—
4·7	0·445	1·34	—	1·2	0·89	0·81	1·17	—
6·15	0·43	1·28	—	1·1	0·86	0·80	1·22	1·40
7·3	0·39	1·21	—	1·0	0·83	0·83	1·21	1·35
8·3	0·29	0·99	—	1·0	0·70	0·70	0·99	1·10
9·0	0·70	0·72	—	,,	—	—	—	0·99
10·6	0·76	0·40	—	,,	—	—	—	0·99
11·8	0·41	0·15	—	,,	—	—	—	0·97

Section b. Germanium and lactate concns. 40 mg.-atoms and 400 mmoles per l. respectively. Solution 75 ml.; 0·5 g. of resin.

pH	Ge	La	Cl	*R* value of free La	$GeLa_3^{2-}$ + La	$GeLa_2^-$ + La	$GeLa^-$ + La
1·25	0·15	0·44	0·79	—	1·09	—	—
1·50 *	0·46	1·38	—	1·7	0·93	0·73	0·99
2·8	0·43	1·415	—	1·5	0·94	0·74	1·10
4·3	0·385	1·35	—	1·3	0·93	0·84	1·14
6·05	0·38	1·335	—	1·1	0·94	0·89	1·26
7·85	0·33	1·24	—	1·0	0·91	0·91	1·24

Section c. Germanium and lactate concns. 120 mg.-atoms and 1200 mmoles per l. respectively. Solution 75 ml.; 0·5 g. of resin.

	Species sorbed; mole or g.-atom per equiv. of resin			Ratio La : Ge in sorbed	Resin capacity, equiv. per equiv. of resin, calculated for	
pH	Ge	La	Cl	complex	$GeLa_3^-$ + Cl	$GeLa_3^{2-}$ + Cl
0·60	0·18	0·54	0·72	2·95	0·90	1·08
0·75	0·28	0·84	0·575	2·96	0·86	1·14
0·90	0·32	0·915	0·505	2·86	0·83	1·15
1·05	0·38	1·12	0·395	2·90	0·78	1·16

* The natural pH of the system.

TABLE 3. *Sorption of germanium and mucate from solutions by Amberlite* I.R.A. 400-Mu.

Germanium and mucate concns. 30 mg.-atoms and 30 mmoles per l. respectively. Solution 100 ml.; 0·5 g. of resin.

	Species sorbed; g.-atom or mole per equiv. of resin			*R* value of	Resin capacity, equiv. per equiv. of resin, calculated for			
pH	Ge	Mucate	Cl	mucate	$GeMu^-$ + Mu	$GeMu^{2-}$ + Mu	$GeMu^{3-}$ + Mu	Mucate and germanate
1·25	0·450	1·36	0·313	0·75				
2·05	0·595	0·89		0·64	1·05	1·63		
3·5	0·505	0·70		0·56	0·87	1·39		
5·0	0·48	0·66		0·53	0·83	1·28		
6·5	0·475	0·62		0·52	0·74	1·23		
7·2	0·47	0·62		0·50	0·75	1·23		1·40
8·8	0·46	0·58		,,	0·70	1·16		1·30
9·6	0·395	0·50		,,	0·60	1·00	1·39	1·15
10·4	0·325	0·43		,,	0·54	0·86	1·18	1·05
11·0	0·295	0·38		,,			1·06	1·06
11·3	0·290	0·37		,,			1·03	1·15
11·4	0·26	0·38		,,			1·00	1·09
11·55	0·295	0·36		,,			1·01	1·16
12·35	0·275	0·38		,,			1·04	1·30

acid (*ca.* 3 g. per l.). This sets an upper limit to the mucate–germanium solution ratio if useful quantities of germanium are to be employed.

In Table 3 are shown results obtained with solutions containing 30 mg.-atoms of germanium and 30 mmoles of mucic acid per l. at different pH values. In the presence of free hydrochloric acid (pH 1·24), when the sorption of free mucate is very small (0·03 mole per equiv. of resin), the ratio mucate : germanium on the resin is almost exactly three. This exclusive sorption of the 3 : 1 ligand–germanium complex by the resin in presence of free hydrochloric acid is similar to what occurs in the lactic acid system, and in contrast to the tartrate system where only the 1 : 1 complex is sorbed under similar conditions. In the pH range 2—10 no one complex satisfies the resin data for more than two consecutive results, and a mixture of complex ions is clearly being sorbed. The most probable explanation of these results is that a 1 : 1 mucate–germanium complex, whose charge increases from one to two over this pH range, is being sorbed by the resin. At pH 11 and above, the results are in accord with the sorption of a trebly charged 1 : 1 mucate–germanium complex. That sorption of free germanate and mucate appears to fit the resin data at pH 10·4 is considered fortuitous and due to the rapidly changing *R* value [12] for germanate between pH 9 and pH 12.

Very similar results have been obtained with solutions containing 30 mg.-atoms of germanium and 50—90 mmoles of mucate per l. between pH 1·4 and pH 11·7, exclusive sorption of the 3 : 1 mucate–germanium complex by the resin again occurring in presence of hydrochloric acid.

Structure of Complexes.—The salient feature of the germanium–tartaric acid system is the stability of the 1 : 1 tartrate–germanium complex, this stability being considered due to the tartrate's acting as a quadridentate ligand. It is considered that, with all three acids studied, the hydrogen atoms are displaced from the tartrate's hydroxyl groups on their interaction with germanium. As the 1 : 1 complex carries a negative charge it cannot possess a tetrahedral configuration (which would imply that it is a derivative of un-ionised orthogermanic acid), and it is suggested that it possesses an octahedral structure with water molecules filling the last two co-ordination positions, the negative charge arising from ionisation of a proton from one of these two water molecules. Such a complex should become doubly charged at high pH values but, as shown by the results given in Table 1, further ionisation is preceded by breakdown of the complex into germanate and tartrate.

The formation of the 3 : 2 tartrate–germanium complex can be envisaged as occurring without disturbing the quadridentate binding of the tartrates, two octahedral 1 : 1 units being linked by the displacement of the two water molecules on each unit by the bridging tartaric acid molecule. The non-occurrence of complexes with higher tartrate : germanium ratios than 3 : 2 is largely accounted for by the fact that formation of such complexes would involve rupture of at least one of the tartrate–germanium bonds of the original 1 : 1 complex. That the charge on the 3 : 2 complex is two, becoming one at low pH values, requires explanation. An octahedral germanium complex with anionic ligands is normally doubly charged, and a binuclear complex such as the 3 : 2 tartrate–germanium species should carry four negative charges. However, the 3 : 2 complex has been detected only at low pH values, so that it is considered that the ionisation of this complex has been partly suppressed.

At high germanium concentrations the 1 : 1 tartrate–germanium complex forms aggregates, yielding polymers Ge_nTa_{n-1}. These are presumably linear, each tartrate acting as a double bidentate group binding two octahedral germanate units (cf. the mannitol–germanium polymers [9]); they differ from the 3 : 2 complex in having terminal germanate rather than tartrate units. The overall charge of one unit per germanium atom implies that, as with the 1 : 1 complex, one of the water molecules on each octahedral germanium has lost a proton.

In the lactic acid system only three complexes appear to occur, the 3 : 1, 2 : 1, and 1 : 1

lactate–germanium species. The 3 : 1 complex is doubly charged and thus possesses an octahedral configuration [cf. the $Ge(C_2O_4)_3^{2-}$ complex (ref. 1)], whilst the 1 : 1 complex probably has a tetrahedral structure (by analogy with the 1 : 1 polyalcohol–germanium complexes[9]). The 2 : 1 lactate–germanium complex can occur in two possible forms, uncharged tetrahedral and charged octahedral. The charged complex has been detected and can be envisaged as possessing a structure similar to that of the 1 : 1 tartrate–germanium complex except that two lactate groups replace one tartrate.

The 3 : 1 mucate–germanium complex observed at low pH values is analogous to the 3 : 1 lactate–germanium complex, and is considered to possess an octahedral structure. The singly and doubly charged 1 : 1 complexes observed between pH 2 and pH 10 are considered to possess octahedral configurations also, as does the 1 : 1 tartrate–germanium complex. With these complexes, interaction occurs between the germanium and both the hydroxyl and the carboxyl groups of the mucic acid. The triply charged 1 : 1 mucate–germanium complex occurs at pH values above that at which carboxyl–germanium bonds break, so that in this complex the germanium is bound only by the hydroxyl groups of the mucic acid. Thus by analogy with the 1 : 1 mannitol–germanium complex,[9] the triply charged 1 : 1 mucate–germanium complex has a tetrahedral structure based on orthogermanic acid, three of the germanium's hydroxyl groups interacting with hydroxyl groups on the mucic acid and leaving the fourth germanium hydroxyl group free to ionise. The extra two charges on the complex arise from the two independently ionised carboxyl groups of the mucic acid. The major difficulty arising with these postulated structures is the necessity for assuming that the 1 : 1 mucate–germanium complex changes from an octahedral to a tetrahedral structure as its charge rises from one to three. However, this might result from the change of the germanium binding through both carboxyl and hydroxyl groups (in the singly and doubly charged complexes) to binding only through hydroxyl groups in the triply charged complexes.

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