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METAL COMPLEXES OF HYDROXY-ACIDS

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1. INTRODUCTION

Metal complexes of hydroxy-acids are of considerable interest in various branches of chemistry and chemical technology. Various hydroxy-acids are able to form such complexes with more than sixty elements of the Periodic System. Investigation of the properties of this group of compounds is still far from complete. Nevertheless, sufficient experimental results are already available for several generalisations to be made concerning the process of complex formation. The present paper deals only with complex compounds of aliphatic hydroxy-acids. The most typical and widespread representative is tartaric acid, and therefore our attention will be concentrated mainly on the tartrato-complexes of metals. In several cases, in order to elucidate the influence of the structure of hydroxy-acids on the chemical properties of the complex compounds, data on the complexes of citric, trihydroxyglutaric, and several other hydroxy-acids will also be considered.

It had been noted during the previous century that, in the presence of tartaric acid, the cations of many heavy metals lost their ability to be precipitated by alkali in the form of insoluble hydroxides, and other characteristic analytical properties had changed. Qualitative investigation showed that these phenomena were associated with the hydroxyl groups of the tartaric acid. Other organic compounds containing hydroxyl groups were also found to develop a similar masking action, but replacement of the hydroxyl groups by basic or acidic groups, such as HS, CN, NH_2, Cl, etc., resulted in a considerable loss of complexing power [1,2]. In this way the special role of hydroxyl groups in complex formation was revealed.

Subsequently, complexes of hydroxy-acids were investigated by a great variety of methods. At first, preparative work played the main part. Later, physicochemical methods of studying complexes in solution acquired increasing significance. Below a brief account is given of the characteristic features of the investigation of hydroxy-acid complexes by various methods.

2. PREPARATIVE METHOD OF INVESTIGATION

The method consisted essentially in the preparation of the complex compounds, their isolation from solution, and subsequent analysis of the products. The tartrato-complexes of most metals are usually readily soluble in water, and precipitation with alcohol was used to isolate them in the solid form. An elementary analysis was then made on the resulting compounds: valuable results were obtained. It was established that tartaric acid (also other hydroxy--acids) forms two groups of compounds with metal cations, depending on the participation of carboxyl and hydroxyl groups in complex formation. The first class of compounds are of the simple salt type, formed by replacing the hydrogen atoms of the carboxyl groups by metal cations; they were generally obtained from acid solutions. Examples are the tartrates of manganese, cobalt, and nickel, represented by the empirical formulae $MnC_4H_4O_6$, [3,4] $CoC_4H_4O_6$, [5] and $NiC_4H_4O_6$. [5-7] The complex nature of these compounds was established later from a physicochemical investigation of the properties of the solutions. The second class comprises complexes whose formation was represented as involving the substitution of metal cations for the hydrogen atoms of the hydroxyl groups. This class includes, for example, compounds of the type $BaCuC_4H_2O_6.xH_2O$, [8] $NaCuC_4H_3O_6$, [9] and $NH_4Al(OH)C_4H_3O_7$, [10] which were usually precipitated only from alkaline solutions. However, it was only in rare instances that replacement of the hydroxyl hydrogens by the metal could be reliably established from the elementary analysis. This question long remained a matter of controversy, and many workers suggested that in these cases basic salts of various compositions were formed without involving the hydrogen atoms of the hydroxyl groups. In this connection the synthesis of lead tartrate from a solution of heavy-oxygen water is of interest. The compound formed under these conditions has the normal isotopic composition, and therefore corresponds to the formula $NaPbC_4H_3O_6$, not $NaPb(OH)C_4H_4O_6$. [11]

The preparative method for investigating complexes of hydroxy-acids had great defects. Elementary analysis gave only the empirical formula of the compound, but no information on its structure. It was only in exceptional cases that tartrato-complexes could be isolated in crystalline form. Separation of the compound from solution usually yielded an oily mass or a gluey precipitate, the chemical individuality of which was doubtful. This was observed, for example, in the preparation of the tartrato-complexes of aluminium [10], iron [12], cadmium [13], copper [9], antimony [14], etc. It was an extremely complicated matter to obtain anhydrous compounds, which made it difficult to establish correctly and unambiguously the structure of the complexes: compounds containing water could always be given either the formula of a basic salt or that of a normal salt containing water of crystallisation. The molecular weight of the complexes could be determined only in rare instances. Therefore the simplest formulae were usually assigned to the compounds, although the formation of viscous substances indicated in many cases that polymerisation was

occurring. The preparative method also gave no information on the interconversion of complexes in solution by change in pH and in concentration, or on their stability.

The results of the preparative work are summarised below in Table 1.

3. PHYSICOCHEMICAL METHODS OF INVESTIGATING COMPLEXES IN SOLUTION

Polarimetric Method

Tartaric acid contains two asymmetric carbon atoms, and its solutions rotate the plane of polarisation of light. Complex formation with metal cations was accompanied by a change in the angle of this rotation, associated with the formation of more optically active reaction products. The polarimetric method has been used to study the tartrato--complexes of copper[15-19], beryllium[20], cadmium[21], boron[22-24], aluminium[25-32], titanium[33], thorium[34], germanium[35], tin[36], arsenic[37], antimony[24,37], bismuth[38,39], molybdenum and tungsten[40-49], uranium[26,50,51], iron[26,52], cobalt[26], nickel[26,53], cerium[54], etc.

The following are the main variants of this method of investigation.

A. Study of rotatory power of aqueous solutions of tartrato-complexes of different concentrations. The aim of these experiments was to determine the effect of dilution on the dissociation of the complexes. It was found in this way that, for example, the specific rotation of solutions of complex beryllium tartrates is practically independent of concentration, and hence that these compounds undergo hardly any decomposition into their component parts on dilution. On the other hand, the tartrato-complexes of boric and arsenious acids were found to exist only in concentrated solution, and to be readily hydrolysed on dilution. Tartrato-compounds of molybdenum and tungsten undergo quite extensive hydrolysis, although it is not complete even in very dilute solutions.

B. Study of variation in rotatory power of complexes with acidity of solution. One of the most widely used methods is the measurement of the angle of rotation in a series of solutions having a constant molar ratio of the metal cation to the hydroxy-acid (usually equimolar) and a variable amount of alkali. These experiments showed that acidity had a marked effect on the polarimetric properties of solutions of the complexes (of bismuth, lead, etc.); the specific rotation varied not only in magnitude but also in sign. Such phenomena were usually attributed to a change in composition or structure of the compounds, although in several cases a satisfactory interpretation of the observed facts could not be found. In most of the earlier work, unfortunately, the pH of the solutions was not usually measured, so that the results are qualitative in character.

C. Determination of angle of rotation as a function of the molar ratio of the reactants in order to establish the composition of the tartrato-complexes in solution. In the earlier work the concentration of tartaric acid was usually kept constant in a series of experiments, only that of the metal salt being varied; later the method of isomolar series began to be used. This variant was of particular value with the tartrato-complexes of molybdenum and tungsten, for which other methods were of little use. The composition of the tartrates of iron, aluminium, etc., has been established by the isomolar series method.

In spite of the large numbers of papers, the field of application of the polarimetric method was limited. It could be used only to study the complexes of hydroxy-acids containing asymmetric carbon atoms. It gave no definite conclusions on the structure of the complexes. Furthermore, the dependence of specific rotation on the molar ratio of the reactants was often found to be too complicated, which resulted in a certain arbitrariness in the interpretation of the experimental results. Thus in a polarimetric study of the tartratoferrate(III) complexes Pariselle[52] found the maximum specific rotation to correspond to equimolar solutions of iron nitrate and tartaric acid: *i.e.* one iron atom was associated with one tartrato-residue in the complex. However, various structural formulae could be suggested with this molar ratio, since the iron could react either with the carboxyl groups or with both carboxyl and hydroxyl groups of the tartaric acid. In an isomolar series of solutions of iron nitrate and sodium tartrate† a minimum rotation at an Na_2T : Fe ratio of 3 : 1, and maxima at ratios of 1 : 1 and 9 : 1 were observed; it was difficult to attribute the latter maximum to the formation of a compound containing the components in these proportions. Similarly complicated relations were observed also with the tartrato-complexes of other metals. Finally, the stability of the complexes in solution could be assessed very roughly.

Absorptiometric and Spectrophotometric Methods

These methods have not been very extensively used mainly because the formation of coloured compounds is not very characteristic of aliphatic hydroxy-acids. Absorptiometric measurements have been employed in studying the tartrato- and citrato-complexes of copper[55-57], vanadium[58,59], chromium[60,61], uranium[62-64], iron[12,65,66], cobalt[67], nickel[55,70,71], and rare-earth elements[68]. In some cases this work enabled not only the composition but also the instability constants of the complexes in solution to be determined.

The composition of a compound was usually determined by measuring the optical density of a series of solutions having a constant concentration of the central ion and a variable concentration of the hydroxy-acid. The isomolar series method was also employed. Both these methods were suitable mainly for determining the composition of complexes in solutions sufficiently acid to prevent hydrolysis of the metal salt. Hydrolysis at higher pH-values was sometimes avoided by adding an additional complexing agent, for example a solution of sodium salicylate in studying the tartrato- and citrato-complexes of iron[65,66] by the isomolar series method. In most cases, however, a suitable auxiliary complexing agent could not be found, which made it impossible to employ the isomolar series method at high pH-values, especially in strongly alkaline solutions.

† *cf.* Job's method of continuous variations [Ed. of Translation].

Electrical Conductivity Measurements

Sometimes the composition of complexes could be established from the break on the conductimetric titration curves of metal salts with hydroxy-acids[55]. Conductivity measurements on isomolar series of solutions have been employed to determine the composition of tartrato-complexes of aluminium[69], gallium[72], thorium[73], and vanadium[58]. In most cases, however, this method has served merely as a qualitative criterion of complex formation. Interaction has been detected in this way in the boric, arsenious, and tartaric acid systems[23,74,75]. In studying complex formation between hydroxy-acids and molybdic and tungstic acids, mixtures of molybdic acid with various hydroxy-acids have been found[76-78] to possess a considerably higher electrical conductivity than the separate components. This effect was not observed, however, with non-hydroxylated carboxylic acids. Hence it was concluded that only organic compounds containing alcoholic groups form complexes with molybdic and tungstic acids, the products being complex acids of considerably greater strength than the original components.

Electrochemical Methods

Polarographic and especially potentiometric methods have proved to be most suitable for investigating the complexes of hydroxy-acids. They have often enabled not only the composition of the complexes to be established but also their stability in aqueous solution to be determined, which is of great importance for the chemical characterisation of these compounds and for their practical application. The polarographic method has been less widely used, since it requires a sufficient rate of dissociation of the complex ion on the surface of the mercury electrode, whereas quite often the dissociation of hydroxy-acids is fairly slow.

The polarographic method has been used to study the tartrato- and citrato-complexes of zinc[79,80], cadmium[80,81] indium[82], lead[83], vanadium[84], bismuth[85], iron[65,86], and several rare-earth elements[87].

The potentiometric method of investigation proved to be the most promising, based on measurement of the activity of the metal ions in a solution of the complex compound. It makes possible a direct estimation of the stability of the complexes. The most convenient technique involved metal-ion activity measurement with a variable concentration of the ligand (taken in great excess) and a constant pH. The composition of the compound was then found from the slope of the straight line obtained on plotting the logarithm of the metal-ion activity against the concentration of the hydroxy-acid. Subsequent study of the variation of the metal-ion activity with pH at a constant ligand concentration showed which groups, carboxyl or alcoholic, were involved in formation of the complexes.

In several cases application of the potentiometric method was restricted by the poor reversibility of the metal electrodes (antimony, etc.).

The potentiometric method has been used to study the tartrato-complexes of copper[74,88-92], zinc[79,80], cadmium[80,93,94], tin[95], lead[79,83,91,96], antimony[91], bismuth[85,97], and iron[65].

Potentiometric pH-titration, used mainly to determine the composition of the complexes, was of less value. It has yielded information on complexes of copper[55,98], beryllium[99], aluminium[100], titanium[36], zirconium[99], thorium[73,101], germanium[36], vanadium[102], antimony[37,103], bismuth[104], uranium[64], iron[65], nickel[55], and cobalt[55]. A noteworthy modification of the isomolar series method is based on measuring the pH of mixed solutions of hydroxy-acids and metal salts, and plotting the deviation from additivity.

The procedure in these determinations was as follows: (*a*) the hydrogen-ion concentrations of solutions of the metal salt of various concentrations were measured; (*b*) the hydrogen-ion concentrations of solutions of tartaric acid of different concentrations were measured; (*c*) the results were used to calculate the total hydrogen-ion concentrations for mixed solutions of the metal salt and tartaric acid; (*d*) the hydrogen-ion concentrations of these mixtures were determined experimentally; (*e*) the increase in hydrogen-ion concentration due to interaction in the system (the deviation from additivity) was calculated from the difference between (*d*) and (*c*). The position of the maximum on the curve (*e*) indicated the composition of the complex. This method has been used to study complexes of beryllium[105], aluminium[69], indium, and gallium[72,106], and to estimate their relative stability in aqueous solution.

Study of Heterogeneous Equilibria

Several variants of the solubility method have been used to investigate hydroxy-acid complexes. One modification consisted in studying the equilibrium between sparingly soluble hydroxides, sulphides, or tartrates of metals and aqueous solutions of the complexes formed by these metals with tartaric and other hydroxy-acids. This has enabled both the composition and the stability of the complexes to be determined. This method has been applied to tartrato- and citrato-complexes of copper[57,107,108], zinc[79,80], lead[109,110], bismuth[97,111], and iron[91]. In some cases sufficiently reliable results were not obtained owing to an unfortunate choice of compound as the solid phase; thus iron sulphide and hydroxide[91] gave colloidal solutions, and their properties changed owing to aging phenomena, etc.

In several cases the composition of the complexes was found in the following manner. In a series of experiments, increasing quantities of the hydroxy-acid solution were added to a solution of the metal salt, and then a solution of ammonium hydroxide or an alkali was added. The molar ratio of the components at which no great formation of insoluble metal hydroxide occurred was regarded as corresponding to the composition of the complex[97,112]. This method is of limited value[113] and sometimes leads to incorrect conclusions. It was shown that correct results could be obtained only when a definite relation existed between the instability constant of the complex and the solubility product of the hydroxide.

Bobtelsky[114] used heterometric titration to determine the composition of the complexes. The principle of this method consists in measuring the optical density of suspensions formed by gradual addition of the hydroxy-acid or a salt thereof to a solution of the metal salt (or conversely). The critical points of incipient turbidity, maximum optical density of the suspension, and complete dissolution of the precipitate were noted on the heterometric curves. The molar ratios of the components corresponding to the critical points indicated the composition

of soluble and insoluble complexes. Thus, in the titration of a neutral solution of sodium citrate with lead nitrate solution, no precipitate was formed until a Pb : Ct molar ratio of 1 : 2 was reached. Further addition of lead nitrate solution caused the appearance of turbidity (first critical point), which intensified until the ratio became 3 : 2, after which the optical density of the suspension remained unchanged (second critical point). It was concluded from these results that a compound $PbCt_2^{4-}$ exists in solution, while the precipitate contains the compound $Pb_2[PbCt_2]$. Titration of this precipitate with sodium citrate solution resulted in dissolution of the former, and the optical density of the suspension diminished. Complete disappearance of the cloudiness corresponded to a molar ratio of Pb : Ct = = 1 : 2, *i.e.* to the formation of a soluble compound $PbCt_2^{4-}$. Similar relations were observed in the heterometric titration of alkaline solutions. This method has been applied to complexes of thorium[101,115], lead[116], cerium[117], etc. During recent years an ion-exchange method[118,119] using radioactive tracers has been increasingly used for the experimental determination of distribution and of shift in equilibrium under the influence of a hydroxy-acid. The chromatographic method for the comparative assessment of the stabilities of complex compounds is worth mentioning. It has been suggested that the criterion of stability should be the volume of ligand solution passed through the column corresponding to the maximum content of the given cation in the filtrate: the smaller the volume of eluent at which the maximum concentration of the metal cation in the filtrate is reached, the more stable is the complex. The concentration of the cations eluted from the column was determined radiochemically.

A promising variant of the solubility method has been the extraction method, based on a study of the equilibrium between an aqueous solution of the metal complex of the hydroxy-acid and a sparingly soluble (in water) compound of this metal in a non-aqueous phase. Such a procedure eliminates the experimental difficulties associated with the variability in properties of the solid phase in the solubility method. The theoretical bases of the method and its practical application to the investigation of hydroxy-acid complexes have been discussed[120–123].

4. COMPOSITION AND STABILITY OF TARTRATO- AND CITRATO-COMPLEXES

Table 1 gives fundamental data on the composition and stability of the tartrate complexes of metals. The stability is expressed as the negative logarithm of the instability constant. The physical meaning of the constant is almost always clear from the composition of the compound; in the case of $M_2Cu(OH)_2C_4H_4O_6$ the instability constant is expressed as follows:

$$\frac{[Cu^{2+}][OH^-]^2[C_4H_4O_6^{2-}]}{[Cu(OH)_2C_4H_4O_6]^{2-}}.$$

When the chemical formula indicates that hydrogen atoms of the hydroxyl groups have been replaced by the metal cation, the negative logarithm of the hydrolytic instability constant[122] is given, corresponding in the case of $MFeC_4H_2O_6$, for example, to the process

$$FeC_4H_2O_6^- + 2HOH = Fe^{3+} + 2OH^- + C_4H_4O_6^{2-}.$$

The following abbreviations are adopted in Table 1: $T = C_4H_4O_6^{2-}$; $T' = C_4H_3O_6^{3-}$; $T'' = C_4H_2O_6^{4-}$; M = alkali metal (potassium, sodium, ammonium). Methods: prep = preparative; rot = polarimetric; sph = absorptiometric and spectrophotometric; cm = conductimetric; cond = electrical conductivity; pol = polarographic; pot = potentiometric involving measurement of the metal-ion activity; pot pH = potentiometric pH–titration; hm = heterometric; soly = solubility; extr = extraction; io = ion exchange; and cr = cryoscopic.

TABLE 1. Composition and stability of tartrato-complexes.

Formula	Negative logarithm of instability constant, $-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
1	2	3	4	5
		Copper		
$Cu(HT)_2$	3.3	sph, soly	pH 2—5	57, 107
$M_2Cu(HT)_4$	—	pol	5.5—6.7	124
CuT	—	cm, sph	1—7	55
M_2CuT_2	5.15; 4,94; 5.4	soly, pot, pol	1—7	108, 92, 81
M_4CuT_3	9.2	pol	7—9	81
$MCu(OH)T$	12.45	pot, soly, pol	7—9	57, 107, 15, 16
$M_4Cu(OH)_2T$	19.14	sph, soly	>10	57, 107
$M_2Cu(OH)_2T_2$	9.85	pol	>10	124
$MCuT'$		prep, sph, cm	7—9	9, 55
$M_4Cu(T')_2$	14.82	pot	>10	91
M_2CuT''	—	prep, pot, sph, rot	>10	8, 125, 126 15, 16, 55
$M_2Cu_3OT_2$	—	pot	CuT + MOH	74
Cu_2T''	—	pot	faintly alkaline	91
$M_2CuT''M_4T''$	—	prep	alkaline	133, 134
$M_2Cu_4T_2'T'$	—	prep, pot pH	neutral	128, 129, 131, 127, 130, 132
$Cu_5(OH)_{10}T_3$	—	pot pH	neutral	88—89
		Silver		
Ag_2T	—	prep	sol., 0.2 g in 100 ml	135
		Beryllium		
$BeT \cdot 3H_2O$	—	prep	$Be(OH)_2 + H_2T$	20
$MBe(OH)T$	—	prep	pH 3.4	136
$M_2Be(OH)_2T$	—	prep	» 9	136
$MBe(OH)_2Be(OH)T$	—	prep	» 9	136
$M_2Be_2OT_2$	—	prep	$Be(OH)_2$ + MHT	137
$M_2Be_4OT_2'$	—	prep	»	137
$MBe_3(OH)T''$	—	prep, rot	»	137, 20
$Be_3OT'' \cdot 7H_2O$	—	prep	$Be(OH)_2 + H_2T$	20
		Magnesium, calcium, strontium, and barium		
$MgT \cdot 4H_2O$		prep	—	135
$Ca(HT)_2$		prep	—	135
$CaT \cdot H_2O$		prep	—	135
$MCaT' \cdot H_2O$		prep	—	138
$SrT \cdot 4H_2O$		prep	—	135
M_2SrT_2		prep	—	138
$BaT \cdot H_2O$		prep	—	135
		Zinc		
$ZnT \cdot 2H_2O$	4.74; 3.35	prep, pol, soly	pH 4—7	139, 80
M_2ZnT_2		prep	acid medium	140
$MZn(OH)T$	7.62	pot, pol, soly	pH 5.5—11	79
$MZnT' \cdot 11M_2T$		prep	alkaline medium	140
$M_2ZnT'' \cdot 11M_2T$		prep	ditto	140
		Cadmium		
CdT	3.21	prep, pot	pH <7	21, 80
M_2CdT_2	3.38	prep, pol	pH <7	81, 141, 142
$M_4Cd_2(OH)_4T_2$	23.05	pot	pH 11—14	93
$MCdT' \cdot H_2O$	—	prep, rot	alkaline medium	21, 142
$MCdT' \cdot xM_2T$	—	prep	pH 8—9.8	141
M_4CdT_2'	—	rot	alkaline medium	21
$M_2CdT'' \cdot 6Me_2T$	—	prep	pH> 9.8	141
		Boron		
$HBOT$	—	rot	acid medium	24
$MBOT$	—	rot		24
$M_2B(OH)T_2$	—	rot		24, 144
M_3BOT; $Me_3BO_3T_2$	—	cond, cr		145
$xM_2O \cdot yMO \cdot zB_2O_3 \cdot tT^*$	—	prep		143, 146, 147
		Aluminium		
$MAl(HT)_4$	—	cond, pH	weakly acid medium	69
$MAlT_2$	—	ditto	neutral medium	63
M_3AlT_3	—	rot	$Al_2(SO_4)_3 + Na_2T$	30
$M_2Al(OH)T_2$	—	rot	acid medium	25, 26
$MAl(OH)T'$	—	prep	ammoniacal medium	10
$M_4Al(OH)T_2'$	—	rot	alkaline medium	25, 26
M_6AlT_3'	—	prep		148
$M_3Al(OH)T''$	—	rot	alkaline medium	28, 29
$M_6Al_4O_3T_3''$	—	prep	ammoniacal medium	149

* M = Ca, Ba, Sr, Cd, etc.

TABLE 1 (cont'd.)

Formula	Negative logarithm of instability constant, $-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
1	2	3	4	5
		Gallium and indium		
$GaHTX_2$	—	cond, pH	acid medium	72
GaTX	—	ditto	ditto	72
$MGaT_2$	—	»	alkaline medium	72
$Ga_2T''X_2$	—	»	pH = 7	72
$InHTX_2$	—	»	acid medium	106
In(HT)T	6.8	pol	pH < 2.6	82
In(OH)T	—	prep	alkaline medium	106
$M_2In(OH)T_2$	18.51	pol	pH > 2.6	82
		Titanium		
$(TiO)_2OT\cdot 7H_2O$	—	prep	acid soln.	150
M TiO(HT)T	10.54	extr	pH 4.6	122
MTiOT′	18.2	»	pH 5.5—6.2	122
$M_4TiOT''_2$	25.39	»	pH 9—9.5	122
		Zirconium		
ZrOT	—	prep	acid soln.	151
M_2ZrOT_2	—	»	$M_2T + Zr(NO_3)_4$	152
$M_2ZrT_4\cdot 8H_2O$	—	»	weakly acid	2
$Zr_3(OH)_8T''\cdot 6H_2O$	—	»	ditto	152
		Thorium		
$M_2ThOT_2\cdot 8H_2O$	—	prep	MHT + $Th(OH)_4$	155
$M_2ThOT''\cdot 4H_2O$	—	prep	alkaline medium	155
$Th_3(OH)_4\cdot T_4\cdot 5H_2O$	—	prep	$M_2T + Th(NO_3)_4$	153, 154, 155
		Germanium		
GeOT	6.15	prep, pot pH, rot	acid medium	36, 35, 156, 157
		Tin		
M_2SnOT_2	—	prep	$Na_2T + Sn(OH)_4$	158
$M_2SnOT''\cdot 5H_2O$	—	prep	alkaline medium	159
Sn : T = 1 : 1 and 1 : 2	—	rot	acid soln.	36
		Lead		
$MPb(HT)_3$	4.7	pot	pH 2.5—5	79
PbT	2.9	prep, hm, pot	acid soln.	160, 161, 116, 96
$M_2Pb(OH)_2T$	14.1	pot	alkaline medium	79
MPbT′	—	prep, rot	pH > 7	161, 162
M_2PbT''	14.38; 14.68 13.5	prep, pot rot	alkaline medium	91, 163, 83
$Pb_2(HT)_2X$	—	pol	pH < 7	164
$M_2Pb_2OT_2$	—	pot	weakly alkaline	74
$M_4Pb_2OT''_2$	—	rot	alkaline soln.	161
$M_2Pb_2T''_2$	—	hm	pH > 7	116
$M_3Pb_2T'T''$	—	hm	pH > 7	116
Pb_2T''	—	hm	pH 8—9.5	116
$M_4Pb_4T''_3$	—	hm	pH > 7	116
		Vanadium		
VO(HT)X	—	cond, sph	pH < 3	58
M_2VOT_2	—	cond, sph	pH > 6	58
M_2VOT''	—	prep, pot pH	alkaline soln.	165, 166, 102
		Niobium		
$H_4Nb(OH)T''_2$	—	prep	acid soln.	167, 168
		Arsenic		
MAsOT	—	cr, rot, cond		74, 75, 37
$MAsO_2T$	—	prep		169
		Antimony		
$Sb(HT)_3$	—	prep	acid soln.	14
$Sb(OH)(HT)_2$	—	prep	ditto	14
MSbOT	11	prep, pot	alkaline soln.	170, 91, 171, 172
SbT′				
M_2SbOMT''	—	prep	alkaline medium	173
Sb_2T_3	—	prep	—	14
$M_2Sb_2O_2T_2$	—	cr, cond	—	74
		Bismuth		
$MBi(HT)_4$	8.3	pot, soly	pH < 4	97
Bi(HT)T	—	prep	acid medium	75, 39, 1
BiTX	—	prep	ditto	75, 39
$M_2Bi(OH)_3T$	31	pot, soly	alkaline medium	97
BiT′	19.66	pot, soly	pH 3.5—5.5	92, 111
$MBiT''$	—	pot, soly	alkaline medium	175
$M(BiO)_2T'$	—	prep	—	176
$M(BiO)_3T''$	—	prep, rot	alkaline soln.	75, 39, 3
		Molybdenum and tungsten		
M_2MoO_3T	—	prep, rot	$K_2T + H_2MoO_4$	41, 49
$M_2MoO_2T_2$	—	ditto		44
M_2WO_3T	—	»	$K_2T + H_2WO_4$	41, 49
$M_2WO_2T_2$	—	»		44
		Uranium		
U : T = 1:1, 1:2, 1:3		sph		62

TABLE 1 (cont'd.)

Formula	Negative logarithm of instability constant, $-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
	2	3	4	5
		Manganese		
MnT	—	prep	—	3.4
M_2MnT_2	2.52	prep, soly	pH 5—7	177, 178, 179
		Iron		
FeTX	7.34	sph	pH 1—3	180
M_2FeT_2	—	prep, rot, pol	$Fe(NO_3)_3 + Na_2T$	181, 52
M_3FeT_3	—	prep, rot	—	12, 52
$M_4FeT'T''$	—	extr	pH 12	121
$MFeT''$	28.48	prep, sph, pot, pol	pH 4—6	182, 183, 12, 52, 86, 65.
$M_4Fe_4O_2T''_3$	—	prep	weakly alkaline soln.	184
$M_4Fe_4(OH)_4T''_3$	—	prep	ditto	185
		Cobalt		
CoT	—	prep	—	5
M_2CoT_2	—	prep	$Na_2T + CoSO_4$	186, 187
MCoT′	—	prep	weakly alkaline medium	186, 187
M_2CoT''	—	prep	alkaline medium	186, 187
		Nickel		
NiT	—	prep	acid medium	6, 5, 7
M_2NiT_2	—	prep		6, 5, 7
M_2NiT''	—	prep		5, 188
		Cerium		
Ce_2T_3	—	prep, rot	pH 3.5—5.5	54, 189, 190
CeT′	—	prep	pH 6.8	190
MCeT″	—	prep	pH 6.8—10.7	190

TABLE 2. Stability of citrato-complexes of metals.

Formula	$-\log K_i$	Method of investigation	Conditions of formation (acidity)	References
$MCuH_2CitHCit$	4	sph, soly	pH 3—5	107, 57
MCuCt	2.95	sph, pot, pol	pH < 7	55
$M_2Cu(OH)Ct$	16.35	sph, soly	pH 7—11	107, 57
$M_4Cu(OH)_2Ct_2$	18.77	sph, soly	pH > 12	107, 57
M_2CuCi	13.22	pot pH	alkaline soln.	191
BeH_2CtX	1.4	io	pH 3—4	192
BeHCt	2.22	»	pH 3—4	192
MBeCt	4.52	»	pH 3—4	192
ZnH_2CtX	3.0	pot pH	pH 3—4.3	193
ZnHCt	4.9	ditto	pH 4—7.3	193
MZnCt	4.25	»	acid soln.	191
$M_2Zn(OH)Ct$	9.4; 10.92	pot, pol, soly	pH 5.5—11	79, 194
M_2ZnCi	7.5; 7.44	pot pH	pH 7.3—8.5	193
CdHCt	3.25	pot	pH < 7	94, 195
MCdCt	3.38	pot pH	acid soln.	191
M_2CdCi	6.23	ditto	weakly alkaline	191
$M_3TiO(HCt)Ct$	11.92	extr	pH 5—6	123
$M_2Sn(OH)Ct$	20.0	pot	pH > 7	95
MPbCt	6.5	—	pH 6.95—7.45	196
$M_2Pb(OH)Ct$	13.72	pot	pH 9—13	197
M_3BiCt_2	14.4	pot, pol	pH 3—6	85
M_2MnCi	8.72	soly	neutral and weakly alkaline soln.	198
FeHCtX	6.3	pot pH	acid soln.	199
FeCt	11.85; 14.55	pot, sph	ditto	199, 66
MFe(OH)Ct	9.4; 9.1	pot pH, pol	pH 4—6.5	199
$M_2Fe(OH)_2Ct$	1.9; 2.6	ditto	pH 6.5—7.5	199
MFeCi	21.6	sph	pH 4—6	66
MCoCt	4.41	pot pH	acid soln.	191
M_2CoCi	7.08	ditto	weakly alkaline	191
MNiCt	4.99	»	acid soln.	191
$M_2Ni(OH)Ct$	13.32	—	alkaline medium	200
M_2NiCi	5.27	pot pH	weakly alkaline	191
M_3YbCt_3	8.0	»	pH 3—6	201
$MYb(OH)Ct$	16.0	»	pH 5—6	201
$M_3Yb(OH)_3Ct$	36.0	»	ditto	201
MYbCi	8.0	»	»	201

Most of the compounds which were prepared contained an indeterminate quantity of water, and therefore the water content is not usually indicated. The column headed "conditions of formation" gives the pH limits within which the given compound is formed. In much of the earlier work the pH was not measured, in which cases this column contains either a dash or an indication of other experimental conditions.

Table 2 gives data on the stability of the citrato-complexes of several metals for comparison. Here Ct denotes the $C_6H_5O_7^{3-}$ ion, and Ci the $C_6H_4O_7^{4-}$ ion.

5. DEPENDENCE OF PROPERTIES OF TARTRATO--COMPLEXES ON FORMATION CONDITIONS

Analysis of the accompanying published data enables the fundamental laws governing the formation of hydroxy--acid complexes to be established with tartaric acid as example.

Composition and Structure of Complexes

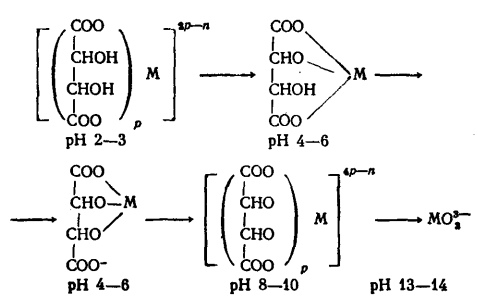
Let us first consider the variation in composition of the complexes with the concentration conditions. Table 1 shows a great variety of composition among the compounds, but nevertheless some general principles can be deduced.

At low ligand concentrations, compounds are usually formed in which one tartaric acid radical is associated with one metal ion, *e.g.*, $CuC_4H_4O_6$, $ZnC_4H_4O_6$, $CdC_4H_4O_6$, etc. These might appear to be simple salts, but they are complex in nature, since they are distinguished by low degrees of dissociation in solution. Increasing the concentration of tartaric acid or sodium tartrate in the system results in coordination by the central metal ion of a further ligand, and sometimes of more than one. Thus at tartrate concentrations up to 0.2 M, the solution contains the mainly undissociated $CdC_4H_4O_6$,[80] while over the range of ligand concentrations 0.2 – 1.0 M a second tartaric acid radical is added to form the complex $M_2Cd(C_4H_4O_6)_2$.[81] Analogous phenomena are observed in several other cases. When the relative concentrations of the central metal ion and of the ligand are unfavourable, if the latter is not present in sufficient excess, more complicated compounds are not infrequently formed at some intermediate pH, in which one metal ion is associated with less than one tartaric acid residue. This applies in particular to salts in which the molar ratio of metal to tartrate is 4 : 3, *e.g.* $M_3Cu_4C_{12}\cdot H_7O_{18}$,[127-129,131,132] $M_6Al_4O_3C_{12}H_6O_{18}$,[149] $M_6Fe_4O_3C_{12}H_6O_{18}$,[184] etc. The chemical individuality of these salts has not been proved in all cases, and perhaps a mixture of more than one substance is isolated. However, there is no doubt about the existence of compounds of this type, at least with copper. Many salts have been prepared[128-130] containing the complex anion $Cu_4C_{12}H_7O_{18}^{3-}$, in which the place of the alkali metal is occupied by complex ammines of cobalt and of several other metals. The bismuth tartrate $K(BiO)_3C_4H_2O_6\cdot 4H_2O$, in which the ratio of bismuth to tartrate is 3 : 1, and which was prepared by Rosenheim[75,39], is worth mentioning.

The principal factor affecting the composition and the structure of the complex tartrates is the pH of the solution. In acid medium, dissociation of the hydroxy-groups of tartaric acid is very difficult, and under these conditions complexes involving only the carboxyl groups are formed predominantly. Examples of such compounds are $Cu(HC_4H_4O_6)_2$,[57,107] $M_2Zn(C_4H_4O_6)_2$,[140] $MAl(HC_4H_4O_6)_4$,[69] $ZrOC_4H_4O_6$,[151] $MPb(HC_4H_4O_6)_3$,[79] and many others. It is evident from the table that they are all formed in acid medium. Raising the pH weakens the bond between hydrogen and oxygen atoms in the hydroxyl groups and favours the partial or complete replacement of these hydrogen atoms by metal cations. This yields complexes in which the metal is directly linked with the oxygen of both hydroxyl and carboxyl groups. An illustration is provided by the formula of the so-called ferritartaric acid $HFeC_4H_2O_6$, which was prepared by Paira[182]. Here the ferric ions have replaced the hydrogen atoms of both hydroxyl groups and of one carboxyl group. Alkali-metal salts of this acid are readily soluble, and their behaviour in solution has been studied by many workers[65,86]; these physicochemical researches have confirmed the correctness of the above formula.

In some cases replacement of the hydroxy-hydrogen atoms by metal still occurs in weakly acid medium. This is characteristic, for example, of the cations of iron[65,52], bismuth[92,111], antimony, and other readily hydrolysable metal cations. As a general rule, however, such substitution takes place most readily in alkaline solutions, where the cations of most metals form complexes of this type. In the pH range 10 – 14 compounds are usually obtained in which the metal is now linked only with the oxygen atoms of the hydroxyl groups. Examples of such compounds are provided by salts having the composition $M_2CuC_4H_2O_6\cdot xH_2O$,[8,15,16,55,125,126] $M_2Al(OH)C_4H_2O_6$,[28,29] $MTiOC_4H_3O_6$,[122] $M_2SnOC_4H_2O_6\cdot 5H_2O$,[159] $M_2PbC_4H_2O_6$,[83,91,163] and $M_2VOC_4H_2O_6$.[102,165,166]

Thus the general picture of the variation in composition and structure of the complexes of tartaric acid with increase in solution pH can be represented, for example for a tervalent metal cation, by the scheme:



The last stage of the process, the formation of soluble hydroxo-salts at high pH-values, occurs quite often with cations of metals having amphoteric properties, as will be shown below.

Some writers[107] have doubted whether the hydroxy-hydrogens of tartaric acid can be replaced by metal cations. They have regarded compounds formed in alkaline solutions as hydroxide (basic) salts, for example $M_2Cu(OH)_2C_4H_4O_6$. It has hardly ever proved possible to obtain such salts anhydrous, and therefore the formula $M_2CuC_4H_2O_6\cdot 2H_2O$ could always be written in the above form. Elementary analysis does not usually enable a distinction to be made between these two formulae, as a result of which two opposite views on complex formation by hydroxy-acids existed for a long time. According to one, complexes are formed by the metal displacing the hydrogen atoms of the hydroxyl groups; according to the other, hydroxide salts are formed under these conditions. However, quite convincing direct and indirect proofs are now available of the correctness of the

view that the metal displaces hydrogen atoms from the hydroxyl groups, including the following. (*a*) Such substitution has been established quite definitely in the case of aromatic hydroxy-acids and alcohols [202]. There is no fundamental difference in this respect between aromatic and aliphatic hydroxy-compounds, although the acidic character of the hydroxy-groups is less marked in the latter case owing to the absence of the aromatic radical; in several cases there is no doubt that the corresponding values of p*K* are greater than 14. It will therefore be somewhat more difficult to replace hydroxyl hydrogen by a metal in aliphatic, than in the corresponding aromatic, hydroxy-acids. (*b*) Derivatives of aliphatic hydroxy-acids in which hydroxyl groups have been replaced by amino- and other groups [2,10] have lost the ability to form complexes. (*c*) Replacement of hydroxy-hydrogen atoms by a metal is indicated by elementary analysis of some complexes; thus ferritartaric acid was shown [182] to contain 27.56% of iron and 23.68% of carbon, which corresponds to the formula $HFeC_4H_2O_6$. (*d*) When lead tartrate and some other tartrate complexes are prepared in solutions of heavy-oxygen water, the precipitated complexes contain [11,203] no heavy oxygen, so that the metal has not combined with the hydroxyl groups of water. (*e*) Dimethoxysuccinic acid HOOC.CH(OCH_3).CH(OCH_3).COOH differs from tartaric acid in forming no complexes with the cations of lead, titanium, copper, or aluminium in alkaline solution; it also behaves differently towards iron cations, forming with them complexes having altogether different properties [180]. These experiments indicate directly the role of the hydroxy-hydrogen in the formation of complexes.

Stability of Complexes

It is clear from Table 1 that instability constants have been determined only for a few tartrato-complexes of metals. Nevertheless, the instability constant is the most important thermodynamic characteristic of a complex compound, and a knowledge of it is necessary for most fields of application of such compounds. An attempt is made below to give a qualitative account of the variation in stability of tartrato-complexes of metals with the acidity of the solution, the properties of the complex-forming cation, and the position of the latter in the Periodic System. This account is based primarily on the data on instability constants in Table 1. Published data on the relative stability of the tartrato-complexes of several metals [204-209] are also taken into account.

The influence of the acidity of the solution on the stability of tartrato-complexes depends on the properties of the central ion. In this respect all elements can be usefully divided into two classes. The first includes tungsten, molybdenum, boron, arsenic, etc., whose oxides have a more or less clearly defined acidic character. Quantitative data on the stabilities of the tartrato-complexes of these elements are lacking. The literature contains qualitative observations indicating that the complexes become less stable with increasing pH. The tartrates of molybdenum, boron, tungsten, and arsenic are formed mainly in acid medium, and decompose into their component parts in alkaline or in neutral solutions [37,49,210]. Such peculiar behaviour of these complexes is linked with the ability of the elements to yield cationic forms only in comparatively acid medium. Increase in solution pH considerably facilitates replacement of the hydroxy-hydrogens of tartaric acid by metal cations; however, the tendency of the cationic forms of these elements to pass into anionic forms, which can no longer interact with tartaric acid, grows to a still greater extent. It has been established, for example, that free tartaric acid shows the greatest tendency to form complexes with molybdenum and tungsten [41-43]; acid tartrates occupy an intermediate position, while a tartrate containing two alkali-metal atoms no longer reacts with molybdates or tungstates. An analogous phenomenon is observed also in the formation of the tartrato-complexes of arsenic. Polarimetric measurements have shown that the complex breaks down into its components on neutralisation with alkali [37,210].

The second class includes elements having basic properties, such as copper, cobalt, nickel, iron, bismuth, etc. Here an increase in pH causes enhanced stability, which is associated with a change in structure of the complexes. On passing from acid to alkaline medium, replacement of the hydroxy-hydrogen atoms by metal cations usually begins, dissociation of the hydroxyl groups being greatly facilitated in alkaline solution. This is the principal reason for the more complete binding of metal cations in complexes with rise in solution pH.

Elements having amphoteric properties — zinc, aluminium, lead, etc. — occupy an intermediate position. Here the stability of the tartrato-complexes at first increases with rise in pH. However, at some intermediate pH the tartrato-complex begins to change into a hydroxide salt, depending on the individual properties of the complex-forming cation. Thus in a solution containing tartrate, zinc exists in the zincate form already at pH ~ 12; [80] the tartrato-complex of lead, however, exists even in solutions of pH > 13. [83]

Difficulties arise in comparing numerical data representing the stabilities of the tartrato-complexes of different elements, because the values of the instability constants quite often relate to compounds of differing composition and structure, and therefore cannot be compared directly. Moreover with many compounds, as mentioned above, the instability constants have not been determined at all. The parameter adopted in Table 3 for comparing stabilities is the logarithm of the degree of binding of the metal cation in the tartrato-complex [204], *i.e.* the logarithm of the ratio of the concentration of metal ions combined in the complex to their concentration remaining uncombined under some standard conditions of acidity; the concentration of the ligand, tartaric acid, was taken as unity in all cases. These numerical values have been determined experimentally [204-207,211], or else calculated from the instability constants.

The accompanying numerical data, together with some qualitative observations in the literature, enable the variation in stability within groups and periods in the Periodic System to be traced. Most of the data relate to alkaline solutions, in which the specific complexing action of tartaric acid, due to combination of the metal cation with the oxygen of a hydroxyl group, is most clearly developed. The stability of the tartrato-complexes at high pH-values is also of interest from a practical point of view, since many cases of masking are in fact based on the formation of complexes in alkaline solutions. The ringed numbers denote logarithms of the degree of binding at pH ~13, and those in rectangles at pH ~ 10; with zinc and cadmium, values of the logarithm are given for the complexes in acid medium (pH 5).

The absence of experimental data makes it impossible to

give a quantitative idea of the variation in stability within Group I of the Periodic System. Copper is combined to quite a large extent; silver probably gives a less stable complex, since alkali precipitates silver hydroxide from tartrate solutions. Comparison of the constants in Group II shows the zinc complex to be rather more stable than the cadmium complex. In Group III the gallium complex is the most stable, those of indium, thallium, and aluminium having a lower and almost identical stability. In the first subgroup of Group IV the stability falls on passing from titanium to zirconium and then to hafnium [209]; and in the second subgroup from tin(II) to lead. A similar phenomenon is observed in Group V, the bismuth complexes being less stable than those of antimony. Even these still very incomplete data enable the general conclusion to be drawn that, within individual groups of the Periodic System, the stability of the tartrato-complexes decreases on passing down the group. This can be related to the ionic radii: it is probably a general rule that the complexes become less stable with increasing radius of the complex-forming cation.

The numbers in Table 3 also enable the variation in stability within the Fourth Period to be traced. Comparison of the stability at pH ~ 13 (ringed numbers) shows a sharp increase in degree of binding on passing from manganese to tervalent iron, followed by a decrease on passing to cobalt and nickel. With copper the stability again increases. Comparison of the stability of the tartrates of aluminium, titanium, iron, and quadrivalent vanadium at pH ~10 shows primarily the considerably greater stability of the tartrato--complex of iron than that of titanium. This is probably due to the difference in charge on the two ions, titanyl and iron.

Few data are available for comparison of the stabilities of complexes in the Fifth and Sixth Periods. Only increases in stability in the order cadmium–antimony, tin–antimony, and lead–bismuth can be noted. Thus the variation in stability of the tartrates within the periods is mainly associated with the ionic charge. With identical ionic charges and radii, the stabilities of the complexes can be linked with the values of the covalency index‡ proposed by Yatsimirskii [212]. The correlation between these quantities for manganese, cobalt, nickel, and copper§ can be seen from the following data:

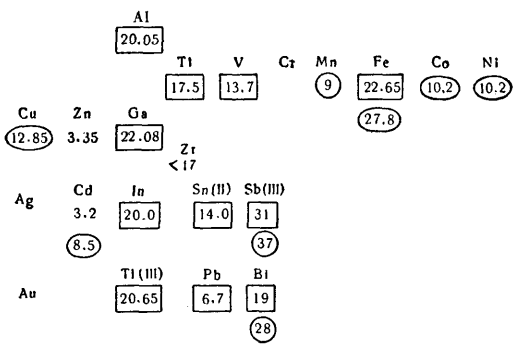
	Mn	Co	Ni	Cu
Covalency index	85	93	97	137
Logarithm of degree of binding	9.0	10.2	10.2	12.85

The stability of metal complexes of tartaric acid is probably determined by those factors which govern the strength of bonding of the metal cation to hydroxyl groups. The order of solubility of the metal hydroxides is in many cases similar to that of the stability of the tartrato-complexes. This point is illustrated by the following data [204], which compare the pH at which hydroxides of the metals

‡ Yatsimirskii defines "covalency index" as the difference between the ionisation potential of an atom and the heat of hydration of the ion derived from it [Ed. of Translation].

§ It is probable that such a relation is not always observed. Thus, while the ionic radii are similar, the covalency index of mercury (226) is considerably greater than the corresponding value for copper, yet qualitative experiments show that the tartrate complex of mercury is not very stable.

TABLE 3. Variation in stability of tartrato-complexes in the Periodic System.



start to be precipitated with the logarithm of the degree of binding of these metals of the tartrato-complexes:

	Fe	Cu	Co	Ni	Mn
pH of start of precipitation	1.6	4.2	6.8	6.8	7.4
Logarithm of degree of binding	27.3	12.85	10.2	10.2	9.0

Analogous trends are observed also with the tartrato--complexes of aluminium, iron, gallium, indium, and thallium [205,207], and the citrato- and trihydroxyglutarato--complexes of manganese, cobalt, nickel, and copper [206]. The readily hydrolysed cations of tervalent antimony form considerably more stable tartrato-complexes than do the cations of bismuth, which show less tendency to hydrolysis. The stability of the tartrato-complexes diminishes also from zirconium to hafnium [209] in conformity with the accompanying decrease in the tendency of the cations of these metals to undergo hydrolysis.

The above correlation between the stability of the tartrato-complexes and the tendency of the corresponding metal cations to undergo hydrolysis can be explained by the analogy between the action of inorganic and organic reagents developed by Kuznetsov [214]. The hydrolysis of metal salts is a manifestation of the tendency to form an M–OH bond by the action of water. Complex formation between metals and organic reagents containing an OH-group, in particular hydroxy-acids, however, reflects, according to Kuznetsov, the tendency to form an M–OR bond under the influence of the reagent H–OR. Such a reagent can be regarded as a derivative of water in which one hydrogen atom has been replaced by an organic radical. The two processes are therefore formally analogous, although the substitution of a complicated organic group for the hydrogen in water can also be reflected in the properties of the reaction product. In particular, this analogy takes no account of chelation involving the metal cation and the organic radical; chelation is not involved in the reaction of a metal cation with water. Nevertheless, this generalisation can be utilised for a rough qualitative assessment of the stability of tartrato--complexes.

6. RELATION BETWEEN STABILITY OF COMPLEXES AND STRUCTURE OF HYDROXY-ACID LIGANDS

Different hydroxy-acids exhibit different powers of complex formation with metal cations. The stability and other

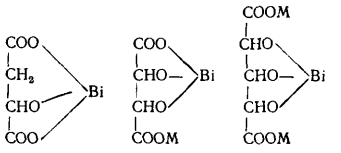
properties of the complexes depend on the numbers of carboxyl and hydroxyl groups in the hydroxy-acid molecule and on their relative positions, on the ability of these groups to dissociate by splitting off hydrogen ions, on the length of the carbon chain, etc. Thus in acid medium, where complex formation is usually due to interaction of the metal cation with the carboxyl groups, the number of hydroxyl groups should have little effect on the properties of the complexes. In alkaline solutions, on the other hand, the number and mutual arrangement of the hydroxyl groups, etc. should be of greatest significance. Too little experimental work has yet been done for a comprehensive consideration of all these factors or a full assessment of their influence on the properties of the resulting complexes. Nevertheless, a few data on this question are available, and are examined in the present section.

The stability of the complexes of tartaric and citric acids can be compared on the basis of the data in Tables 1 and 2. The physical significance of the instability constants of the complexes of the two hydroxy-acids differs, and therefore they cannot be compared directly. It is best, as in the preceding section, to use the degrees of binding as measures of stability.

Let us first examine the relation between the stabilities of the complexes in acid solutions. The citrato- and tartrato-complexes of titanium have been compared[123] using this criterion of stability. That of the citrato-complex of titanium at pH ~ 5 was found to be approximately two orders of magnitude greater than the stability of titanium tartrate, the difference in stability diminishing with rise in pH of the solution. Similar observations have been made for the tartrato- and citrato-complexes of iron[65,66], bismuth[85,92,111], manganese[215], yttrium, and cerium[216]. The masking action of citric acid on the precipitation of the cations of beryllium, vanadium, antimony, cobalt, and nickel by organic precipitants is also considerably more marked in acid solution than is the masking effect of tartaric acid[217]. Thus it follows from these data that citrato--complexes are more stable than the tartrato-complexes. This can be related to the number of carboxyl groups in these hydroxy-acids, which play the main part in complex formation in acid solution. In the case of citric acid the cation (for example of a tervalent metal) is able, by combining with three oxygen atoms in the carboxyl groups, to complete two seven-membered rings, whereas in the case of tartaric acid only one such ring can be formed, which, of course, affects the stability of the complexes.

A different relation is observed in alkaline solutions. Here citric acid usually forms less stable complexes than does tartaric acid. Sodium tartrate has a far stronger masking action than has sodium citrate on the precipitation of the 8-hydroxyquinolinato-complexes of beryllium, titanium, lead, bismuth, and iron; the 1-nitroso-2-naphthol complexes of copper; lead ethyl xanthate; and indium and bismuth diethyldithiocarbamates[217]. The degree of binding of iron in the tartrato-complex has been shown[121] to be about 900 times greater than that in the citrato-complex. Trihydroxyglutaric acid, which contains three hydroxyl groups, gives still more stable complexes under these conditions. An analogous relation is observed on comparing the stabilities of the copper, cobalt, and bismuth complexes in the series trihydroxyglutaric–tartaric–malic acids[218]. The stability of the complexes of all three metals falls in this order.

These phenomena have been explained[121,218] on the basis of the possibility of a larger or a smaller number of closed five-membered rings being formed involving the metal cations and the hydroxyl groups of the acids. Such closed rings probably possess greater stability than analogous rings formed by the metal cations with the carboxyl groups. In alkaline solutions, therefore, where complex formation involves the hydroxyl groups, complexes of hydroxy-acids containing a large number of such groups are the most stable. Thus the complexes formed by bismuth with malic, tartaric, and trihydroxyglutaric acids can be represented by the following structural formulae:



It is seen from these formulae that the greatest stability shown by the trihydroxyglutarato-complex of bismuth may be due to the formation of two chelate rings involving three hydroxyl groups. The tartrato-complex of bismuth is less stable, since the two hydroxyl groups of tartaric acid are able to give only one chelate ring with the bismuth ion. In the case of the malato-complex there is no such chelate ring formed solely by hydroxyl groups, and therefore the complex has the lowest stability. In the citrato-complex of iron the possibility of the formation of a chelate ring involving hydroxyl groups is excluded; the hydroxyl groups of tartaric acid can now form one such ring with iron cations, while in the case of trihydroxyglutaric acid two such rings can be formed. The stability of the complexes also varies in conformity with this.

7. APPLICATION OF COMPLEXES OF TARTARIC AND OTHER HYDROXY-ACIDS IN ANALYSIS

Hydroxy-acids form complexes by replacement of the hydrogen atoms in the carboxyl or hydroxyl groups with metal cations. This affects the acidity of the medium, and quite often simple stoichiometric relations exist between the quantity of hydrogen ions liberated and the quantity of metal ions combined in the complex. This property is utilised in analytical chemistry for the direct determination of several metals by acid–base titration. Some analytical applications exploit the change in absorption spectrum of the metal cations accompanying complex formation, although aromatic hydroxy-acids are most often employed for this purpose. However, the main field of application is based on the ability of tartaric and citric acids to form with the cations of different metals complex compounds of differing stability, and thus to exert a differentiating action on various properties of the elements. This differentiating effect is employed for the separation of rare-earth elements on a chromatographic column, for the chemical separation of elements, for the analytical determination of a mixture of cations of several metals by electrochemical methods, etc.

Utilisation of Acid–Base Properties of Complexes

Methods have been described for the determination of zinc[219,220], cadmium[221], aluminium[112,222], titanium and zirconium[223], cerium[224], tin[225,226], lead[213], chromium[227], iron[228–230], manganese[231], and cobalt[232], based on titration of the acid liberated when these metal cations react with the alkali-metal salts of tartaric and other hydroxy-acids.

Interesting methods for the determination of beryllium and aluminium [233,234] are based on titration of the alkali produced when tartrato-complexes of these elements react with sodium fluoride solution:

$$M_2BeC_4H_2O_6+2H_2O+4MF=M_2BeF_4+M_2C_4H_4O_6+2MOH.$$

In certain special cases these methods possess several advantages, in particular a considerable economy of time. However, they are not very accurate. Quite often the reactions are not completely stoichiometric, and therefore various empirical coefficients must be used in calculating the analytical results. The change in colour of the indicator at the end-point is not usually sufficiently sharp. Moreover, direct determinations are impossible in solutions containing free acid. All these facts considerably limit the widespread use of these methods for the analytical determination of elements.

Formation of Coloured Compounds

Copper, vanadium, chromium, iron, cobalt, and nickel give coloured complexes with tartaric and citric acids. These complexes are characterised by low molar extinction coefficients, and are not very suitable for use in colorimetry. Nevertheless, methods have been described in the literature for the colorimetric determination of the cations of several metals by means of tartaric and citric acids. A method has been suggested [235] for the spectrophotometric determination of iron in the ultra-violet by means of tartaric acid, and a procedure has been worked out for determining iron in rocks by this method. Nickel, cobalt, and copper can be determined when present together [236] by measuring the light absorption in different spectral regions of the complexes formed in alkaline tartrate solutions. The intense dark blue colour of vanadium citrate has been utilised [237] for the colorimetric determination of this metal. Tartaric, citric, and some other hydroxy-acids can be determined quantitatively [238] from the fading which they produce in the colour of ferric thiocyanate solution.

Use of Hydroxy-Acids as Masking Agents

Several examples of the masking action of hydroxy-acids are well known. Thus iron is separated from titanium and aluminium by precipitation with hydrogen sulphide from alkaline solution while the latter elements are masked with tartaric acid. On the other hand, iron is masked with tartaric acid for separation from nickel, which is precipitated with dimethylglyoxime. Aluminium is masked with sodium tartrate while bismuth is precipitated with ammonium sulphide. The use of sodium citrate has been suggested [239,240] for a sharper separation from one another of cations in the chloride subgroup of the fourth analytical group, for keeping titanium in solution during the precipitation of phosphorus with ammonium molybdate [241], and for eliminating the effect of aluminium and zinc on the complexometric determination of iron in their presence [242]. A technique has been worked out [243] for separating beryllium from aluminium, iron, copper, and chromium by precipitating it with ammonium hydroxide from tartrate solution. Masking with tartaric acid has been employed in the separation of niobium and tantalum from titanium [244,245], and of tantalum from niobium [246].

Use of Hydroxy-Acids in Electrochemical Methods of Analysis

Reference must first be made to the great value of hydroxy-acids in electroplating and electroanalysis, where they are used to improve the quality of the coating and to obtain dense deposits of metal on the electrodes. This effect of hydroxy-acids is usually attributed to the formation of complexes with the cations of the metals undergoing deposition. It is observed in the electrodeposition of copper and silver [247]. Citrate solutions have been suggested for the electrodeposition of cobalt–tungsten–molybdenum alloys [248]. Masking with tartaric acid is used in the electrolytic separation of tin and antimony [249], and of nickel and zinc [250].

In the polarographic determination of inorganic ions, tartaric and citric acids are often used as supporting electrolytes, with the aim of forming complexes of these ions in order to obtain separate waves for ions present in a complicated mixture and having identical or similar half-wave potentials. The addition of solutions of hydroxy-acids has been shown, by determination of the half-wave potentials of metal cations with such acids as supporting electrolyte, to produce unequal negative shifts in the potentials of different ions and to create conditions for the simultaneous determination of several ions [251,252]. The tartaric-acid supporting electrolyte proved to be suitable for the simultaneous polarographic determination of copper and bismuth [253], which have almost identical half-wave potentials when dissolved in nitric or sulphuric acid, and for the determination of copper, bismuth, cadmium, lead, and zinc as impurities in metallic tin [254], copper, and iron [255]. Citric acid has been used as supporting electrolyte in the polarographic analysis of aluminium, magnesium, and phosphor bronzes [256]. In tartaric-acid and citric-acid solutions, separate waves have been obtained for nickel and cobalt [257], and for iron and titanium [258], and titanium has been determined in aluminium alloys [259]. Solutions of sodium tartrate and citrate have been employed also as supporting electrolytes in the polarographic determination of indium [260], molybdenum [261,262], tin [263–265], and bismuth [266].

Use of Hydroxy-Acids in Chromatography

The main application of hydroxy-acids in chromatography is their use for the separation of rare-earth elements. This problem has recently acquired great commercial importance in connection with the ever-increasing consumption of these elements in metallurgy [267,268] and other branches of industry.

The chromatographic separation of the rare-earth elements is based to a considerable extent [269] on the differing stabilities of their citrato-complexes. When a solution of citric acid is passed through a chromatographic column elements of higher atomic weight pass most readily into solution, since they are able to form more stable citrato--complexes than are elements of lower atomic weight. Thus in the elution of praseodymium and neodymium, ions of the latter are the first to react with the citric acid, and a pure or considerably enriched solution of neodymium citrate flows out of the column, whereas all or a large part of the praseodymium remains adsorbed on the cation--exchange resin.

A quantitative theory of the extraction of rare-earth cations from a chromatographic column with citrate solutions

has been worked out by Spedding[270]. Several papers on the separation of rare-earth elements have been published[271-273] in the foreign press. It has been shown, for example, that thulium can be separated from erbium and ytterbium[274] by elution with citric acid solution. A similar method is used to separate samarium and niobium[275], zirconium and hafnium[276], etc.

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Research on the complex compounds formed by metals with hydroxy-acids cannot be regarded as complete. Many problems require more thorough study. Thus more complete data are necessary on the stability of the complexes, on the relation between their properties and the position of the central atoms in the Periodic System, and also their dependence on the structure of the hydroxy-acids, etc. In some other directions hardly any work at all has yet been done. Several results indicate, for example, that colloidal solutions are formed in some intermediate pH ranges, especially when the concentration of the central ion is considerable and the excess of hydroxy-acid is insufficient. In this case the salts of the hydroxy-acids act as peptising agents towards the insoluble hydroxides of the metals. These phenomena have been little studied, and the interconversion of colloidal particles and complex molecules is of great interest for an understanding of the chemistry of complex formation. It has also been found[277] that, under certain conditions, complex compounds are obtained in solution containing two different central atoms; as yet, the formation of such ternary tartrato-compounds is known only with copper and aluminium. It is probable that other hydroxy-acids and other central atoms are also able to form compounds of this type, and it would be interesting to study them in greater detail. Finally, it has recently been discovered that tartrato- and citrato-complexes of some metals can be extracted by organic solvents in the presence of substituted organic amines[278]. This field has not been studied at all, and merits close attention.

More thorough investigations on the above lines will undoubtedly lead to the discovery of interesting new facts, which will be of both theoretical and practical value.

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