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STEREOCHEMISTRY OF TARTRATO(4-)-BRIDGED BINUCLEAR COMPLEXES

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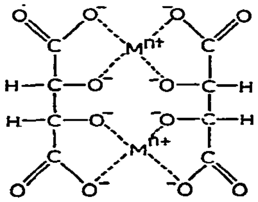
A. INTRODUCTION

The dihydroxydicarboxylic acid, tartaric acid, and its anions react readily with metal ions to form a variety of complexes, many of which are well-known (tartar emetic, Fehling's solution, boro- and ferric tartrates, etc.) and have well-characterized properties. Despite extensive investigations, however, the structures of most metallotartrates have remained extremely uncertain. This uncertainty, for the most part, is a result of 1) the presence of several possible coordination sites in the tartrato ligand, 2) the presence of four potentially ionizable protons in tartaric acid, and 3) the possibility of—and perhaps tendency towards—molecular association owing to the polydentate nature of the tartrate group. Thus the tartrate group atoms which are actually coordinated, the state of ionization of the ligand, and the degree of aggregation of the coordinated species are still uncertain for a great many of the tartrato complexes, although a multitude of structures have been proposed. This problem, with ample reference to early work, has been discussed by several authors[1-3].

Since 1964, several X-ray structure determinations and chemical investigations have shown the existence of a stereochemically unique binuclear structure for tartrato complexes of antimony(III) and vanadyl(IV). Investigations have also implied the presence of a similar structure for two chromium(III) tartrate derivatives. The anionic complexes contain two metal ions bridged by two tetradentate tartrato(4-) ligands. (The tetranegative ligands are formed from tartaric acid when all the carboxyl and hydroxyl groups have been ionized.)

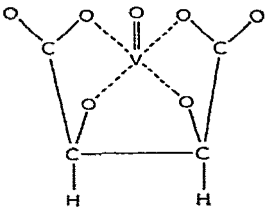


In this article, we shall discuss the stereochemistry of these tartrato(4-) bridged dimers. The geometries of the various vanadyl(IV) and antimony(III) tartrate complexes will first be examined separately and then compared with each other and with the geometries of related compounds whose structures are known. The possible isomers, both known and unknown, and their related stabilities will also be discussed. Possible reasons for the geometrical differences among the various tartrato(4-) complexes and for the relative stabilities of the isomers will then be presented. In so doing, we will have occasion to examine the conformations and geometries determined for the tartrate groups in other tartrate compounds. Finally, evidence indicating the existence of similar tartrato(4-)-bridged binuclear species in other metallotartrate systems will be cited and discussed.

B. VANADYL(IV) TARTRATES

(i) *Chemistry and properties*

The 1:1 complex formed by tartrate ion and vanadyl(IV) ion (VO^{2+}) in aqueous solution above pH 7 can be isolated as salts having the empirical formula $M^{n}_{2/n}[VO(C_4H_2O_6)] \cdot xH_2O$, where M is a univalent or divalent cation[4–7]. Although various states of ionization were proposed for the tartrate group in these complexes[8,9], the stoichiometries of the salts isolated, spectral studies[10], and potentiometric titrations of vanadyl(IV) tartrate solutions[11] indicated that the tartrate ligand was both tetranegative and in a quadridentate coordination to the vanadyl(IV) ion. Until recently, the complex was usually assumed[12] to consist of a vanadyl(IV) ion, around which was wrapped the tartrato(4-) group to give the square-pyramidal coordination geometry which has since been found to be characteristic of most vanadyl(IV) compounds[13–19, 137]:



Molecular models, however, indicated that a monomeric 1:1 vanadyl(IV) complex containing a quadridentate tartrate group would be impossibly strained for any reasonable geometry about the vanadyl(IV) ion[20]. Moreover, spectral differences between aqueous solutions of vanadyl(IV) ion with active and racemic tartaric acids at about pH 7 showed that the 1:1 anionic complexes present could not be monomeric[20,21]. Based upon molecular weight determinations, e.p.r. spectra, and potentiometric titration data, tartrato(4-)-bridged binuclear structures were proposed for the tartrato complexes present in the active (Fig. 1) and racemic (Fig. 2) solutions[20]. The essential features of these proposed structures have recently been verified by X-ray structure determinations on the salts $(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$[22] and $Na_4[(VO)_2(d\text{-tart})(l\text{-tart})] \cdot 12H_2O$[23], where "tart" designates the tartrato(4-) ($C_4H_2O_6^{-4}$) ligand.

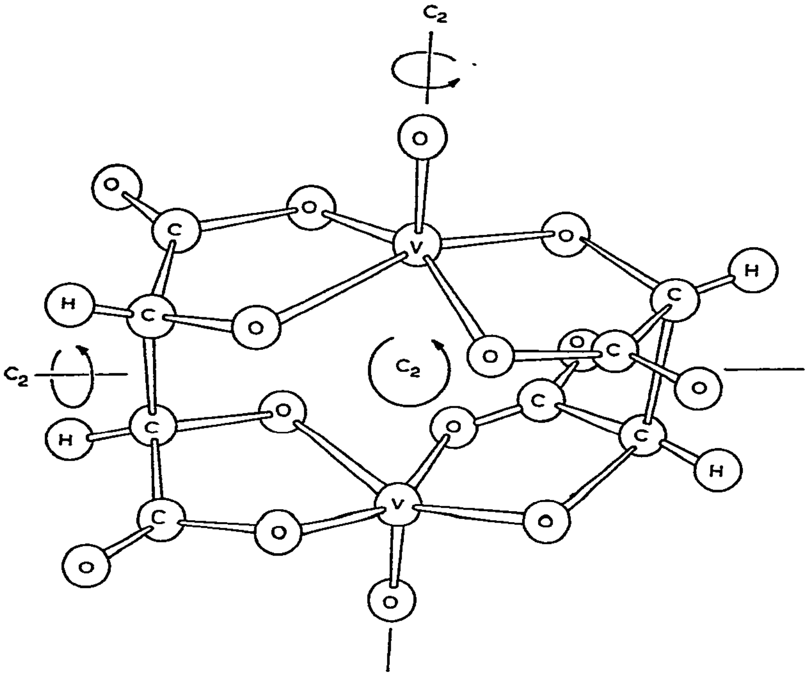


Fig. 1. Idealized geometry for the $[(VO)_2(d\text{-tart})_2]^{4-}$ (active) complex.

(ii) *Structure*

The vanadyl(IV) tartrate complex formed with active (*d*) tartaric acid contains two *d*-tartrato(4-) bridging groups whereas that formed with racemic (*dl*) tartaric acid contains two bridging groups of opposite enantiomeric form. For convenience, these isomeric forms will be referred to as *dd* and *dl*.

If all chemically equivalent bond lengths and bond angles were equal, the *dd* isomer would possess D_2 symmetry with three mutually perpendicular twofold rotation axes (Fig. 1). Only the rotation axis perpendicular to the central carbon–carbon bonds of the bridging groups is required by crystallographic symmetry for the anionic complex[22] found in $(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$. Therefore, the two tartrato groups in the dimer are unrelated by symmetry, although each possesses C_2 symmetry. The angle of 177.3 deg. (calculated from the atomic positions reported for the ammonium salt) between either vanadyl group and the vanadium–vanadium vector shows that the VO^{2+} ions are approximately collinear. Collinearity of the vanadyl(IV) groups is required for perfect D_2 symmetry.

A *dl*-type dimer ideally would be centrosymmetric with symmetry C_{2h}, the twofold rotation axis passing through the central carbon–carbon bonds of the tartrato(4-) bridges (Fig. 2). The anionic complex found in $Na_4[(VO)_2(d\text{-tart})(l\text{-tart})] \cdot 12H_2O$, however, is required by crystallographic symmetry to have only

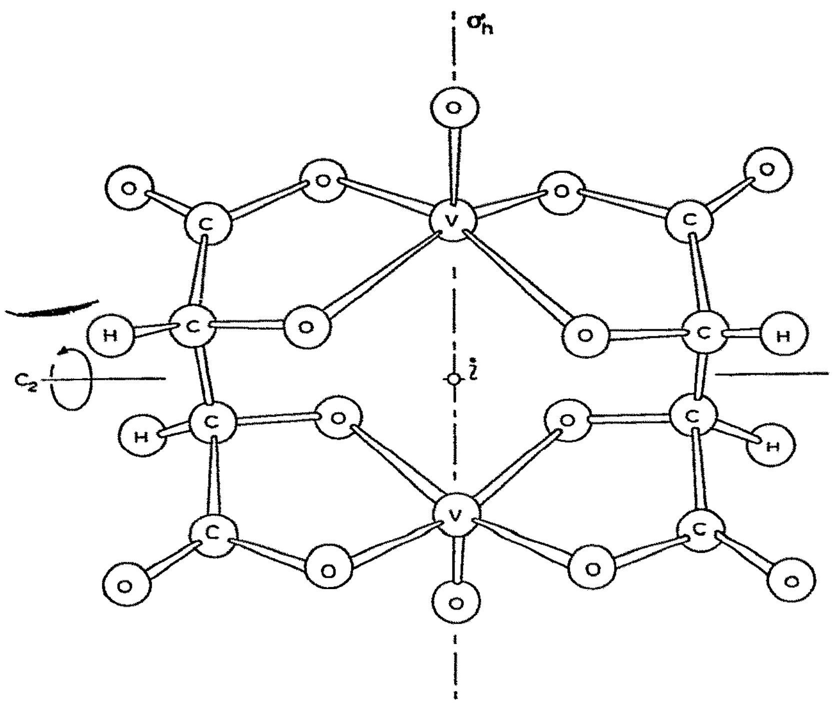
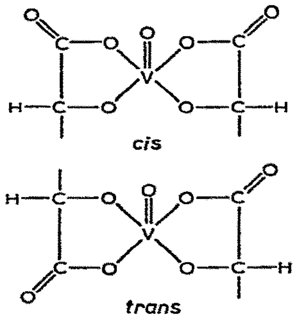


Fig. 2. Idealized geometry for the [(VO)$_2$(*d*-tart) (*l*-tart)]$^{4-}$ (racemic) complex.

an inversion center. Molecular models indicate that the vanadyl ions in the racemic complex will be parallel but not collinear. This prediction is supported by the observed vanadyl oxygen–vanadium–vanadium angle of 152.1 deg. in the *dl* isomer[23].

The presence of two different tartrate enantiomers and the restrictions imposed by the binuclear structure require the *dl* dimer to have a *cis* coordination geometry about the vanadium atom (Fig. 3). A *trans* coordination in a vanadyl(IV)



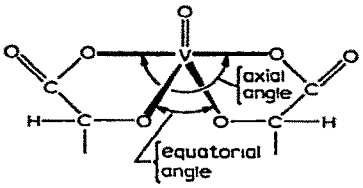


Fig. 3. *Cis* and *trans* coordination geometries of the *dl* and *dd* vanadyl(IV) tartrate dimers.

Fig. 4. Pseudo-trigonal-bipyramidal coordination geometry (exaggerated) of the *dd* isomer of vanadyl(IV) tartrate.

dimer bridged by one *d*- and one *l*-tartrato(4-) ligand is impossible for any reasonable geometry for the complex. On the other hand, the presence of two ligar 's of the same enantiomeric form requires a *trans* coordination geometry in the *dd* (or *ll*) complex.

In addition, there is another dissimilarity between the coordination geometries of the active and racemic vanadyl(IV) tartrate species. As is found in the majority of vanadyl(IV) complexes[13–19], the *dl* anionic complex of sodium vanadyl(IV) tartrate exhibits an approximately square-pyramidal coordination geometry[23]. The coordination geometry determined for the *dd* isomer in the ammonium salt, however, is decidedly distorted from a square pyramid and, in fact, resembles a trigonal bipyramid with the hydroxyl oxygen atoms and the vanadyl oxygen atom occupying equatorial sites and the coordinating carboxyl oxygen atoms occupying[22] axial positions (Fig. 4). Similar distortions from a square pyramid have been found by X-ray structure determinations in only three other vanadyl(IV) compounds — dichlorobis(trimethylamine)oxovanadium(IV), in which the bond angles describe an almost perfect trigonal bipyramid with the trimethylamine groups axial and the chlorine and vanadyl oxygen atoms equatorial[24]; vanadyl(IV) pyridine-2,6-dicarboxylate tetrahydrate, which is also *trans* but has a sixth coordination and exhibits only a small distortion[25]; and the mixed sodium-tetraethylammonium salt of dibenzilato(2-)oxovanadium(IV) diisopropanolate[26]. The latter structure is of particular interest since the complex contains two fully ionized benzilic (diphenylglycollic) acid groups coordinated *trans* with a distorted coordination geometry somewhat similar to that found in the *dd* vanadyl(IV) tartrate isomer. It should be noted that the vanadyl(IV) dibenzilate anionic complex is the only

TABLE 1

COORDINATION GEOMETRIES OF VANADYL(IV) α-HYDROXYCARBOXYLATES[a]

Compound	*Bond angle*[b]		*Bond length*[b]		*Ref.*
	Axial	*Equatorial*	*Axial*	*Equatorial*	
Perfect trigonal bipyramid	180	120			
$(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$	161.9(7)	123.2(7)[c]	2.01(2)	1.79(2)	22
			2.03(2)	1.93(2)	
$Na_4[(VO)_2(d\text{-tart})\,(l\text{-tart})] \cdot 12H_2O$	143.7(2)[d] 150.5(2)		2.004(6)[d] 1.994(5) 1.902(5) 1.917(5)		23
$Na[(C_2H_5)_4N]\,[VO(benz)_2] \cdot 2iso$[e]	151.6(5)	132.9(5)[c]	1.970(9)	1.900(8)	26
			1.971(8)	1.933(8)	

[a] See Fig. 4 for definition of axial and equatorial parameters. [b] Bond angles are in degrees and lengths, in Ångstroms. The e.s.d. of the last figure is in parentheses. [c] Calculated from the reported atomic positions and standard deviations. [d] Since the racemic vanadyl(IV) tartrate complex is approximately square-pyramidal, the designations "axial" and "equatorial" do not apply. The angles given are the *trans* bond angles. The first two bond lengths involve carboxyl and the second two, hydroxyl oxygen atoms. [e] Sodium tetraethylammonium dibenzilato(2-)oxovanadium(IV) diisopropanolate.

complex containing a fully ionized (*i.e.*, both the hydroxyl and carboxyl protons are missing) α-hydroxycarboxylate ligand whose structure has been determined by X-ray methods other than the tartrato(4-) complexes of vanadyl(IV) and antimony(III) discussed herein.

Table 1 presents some of the coordination bonding parameters found for the three vanadyl(IV) α-hydroxycarboxylates whose structures have been determined. In both the *dd* tartrato(4-) and the dibenzilato(2-) complexes, the carboxyl oxygen atoms are pseudo-axial, and the hydroxyl oxygen atoms are pseudo-equatorial.

As Table 1 shows, the active tartrato(4-) complex is very definitely distorted toward a trigonal-bipyramidal coordination geometry, while the racemic tartrato(4-) complex is approximately square-pyramidal. The dibenzilato(2-) derivative exhibits a geometry intermediate between those of the two tartrato(4-) isomers. These differences will be discussed later in this article.

The hydroxyl oxygen–vanadium bond lengths cited in Table 1 are significantly shorter than the carboxyl oxygen–vanadium bond lengths. In fact, the vanadium–hydroxyl oxygen distances of about 1.9 Å in these complexes are significantly shorter than any other vanadium–ligand distance reported[13–19,24,25,137] for a vanadyl(IV) complex (excluding the vanadyl group bond length) with the single exception[27] of V_2O_4, in which a sharp distinction cannot be drawn between the vanadyl group and other vanadium–oxygen pairs. The very short coordination distances involving the ionized hydroxyl group imply a strong *trans* perturbation in the active vanadyl(IV) tartrate complex and the unusual splitting of the *d-d* absorption bands exhibited by this isomer has been explained accordingly[26,28].

(iii) *Isomer stabilities*

The structural differences between the *dd* and *dl* vanadyl(IV) tartrate dimers result in significant dissimilarities in their optical and e.s.r. spectra and stabilities. It is clear that the racemic complex is more stable than the active one[20], since otherwise the *dl* dimer would disproportionate in solution to give a racemic (*dd* and *ll*) mixture, which would not differ significantly from a solution containing only the *dd* (or *ll*) form[142]. Contrary to what is often expected for diastereoisomeric systems[21], large spectral differences are observed between the *dd* and *dl* isomers. It is apparent, therefore, that when polynuclear species are present, stereospecific[143] effects can cause large differences in the properties of diastereoisomeric complexes.

Since tartaric acid also has a *meso* isomer (Fig. 5), there is the possibility of other vanadyl(IV) tartrate isomers containing *meso*-tartrato(4-) bridging groups—the enantiomeric pair *meso-d* and *meso-l* (both of which would contain one vanadyl(IV) ion in a *trans* coordination and one in a *cis* and neither of which could exhibit any symmetry elements) and an optically inactive *meso-meso* dimer. The last isomer would provide interesting possibilities for isomerism since both *cis* (C_{2v} symmetry) and *trans* (C_{2h} symmetry) forms are sterically feasible (Fig. 6).

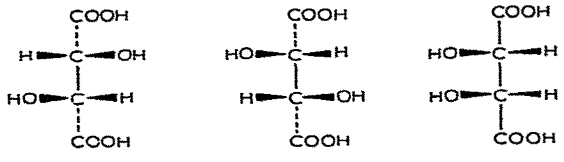
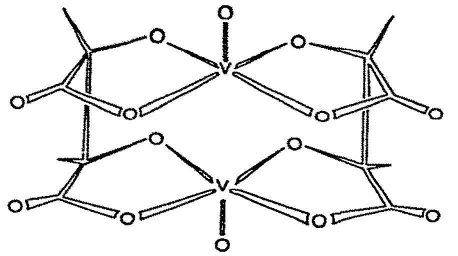

d *l* *meso*

Fig. 5. Isomers of tartaric acid.

Attempted syntheses and potentiometric titration studies, however, imply that vanadyl(IV) binuclear species containing *meso*-tartrato(4-) groups are non-existent or at least very unstable[28,29]. Thus the apparent stability ordering for the various isomers of vanadyl(IV) tartrate is *dl* > *dd* > *meso-meso*, *meso-d*, or *meso-l*.


cis

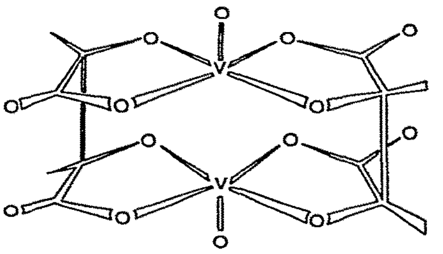

trans

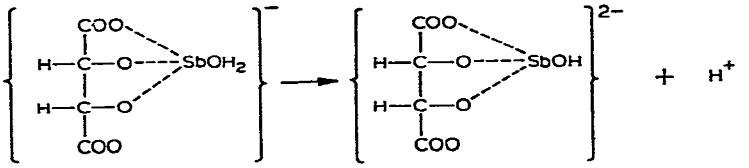
Fig. 6. Hypothetical *meso-meso* tartrato(4-)-bridged vanadyl(IV) dimers.

C. ANTIMONY(III) TARTRATES

(i) *Chemistry and properties*

The structures of tartar emetic (potassium antimony tartrate—a compound of pharmaceutical importance for over 300 years[30]) and other antimony(III) tartrate salts have, until very recently, been vigorously debated[3,30–33]. Ordinary tartar emetic is often referred to as potassium antimonyl tartrate[31]; however, for some time it has been generally accepted that there is no discrete antimonyl (SbO^+)

ion present[3,34]. Based upon the empirical formula $KSbC_4H_5O_{7.5}$ for solid crystalline tartar emetic, structural formulae such as $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ (ref. 35, 36), $K(SbOH)C_4H_3O_6 \cdot \frac{1}{2}H_2O$ (ref. 37), and $KSb(H_2O)C_4H_2O_6 \cdot \frac{1}{2}H_2O$ (ref. 38), or $KSbC_4H_2O_6 \cdot 1\frac{1}{2}H_2O$ (ref. 39), (containing, respectively, dinegative, trinegative, and tetranegative tartrate groups) have been proposed. That antimony(III) would form hydrolytically stable complexes at higher pH only with carboxylates which contained α-hydroxy groups indicated that one or both of the tartrate hydroxy groups were ionized and coordinated[40,41], a conclusion which has also been reached by examination of potentiometric titration data[42]. The structure until recently generally accepted[3,31] for the anionic complex present in tartar emetic was that which was proposed by Reihlen and Hezel—namely, a monomeric species containing a tetranegative tridentate tartrate ligand[38]. The observed acidity of tartar emetic solutions was explained by proposing that a fourth antimony coordination site was occupied by a water molecule capable of ionizing in solution[38]. Other explanations for this acidity have, however, been advanced[37,43].



In 1964, an X-ray structure determination (the first on any tartrate complex) showed the presence of a tartrato(4-)-bridged binuclear complex in racemic ammonium antimony(III) tartrate[44], *dl*-$(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O$. This compound should therefore be designated as racemic diammonium di-μ-tartrato(4-)-bis(antimonate(III)) tetrahydrate, although for simplicity we will simply refer to it as racemic ammonium antimony(III) tartrate. Additional X-ray structure investigations have since determined that tartrato(4-)-bridged complexes are also present in several other antimony(III) tartrate salts—namely, *l*-tris(1,10-phenanthroline)-iron(II) antimony(III) *d*-tartrate octahydrate[45], *l*-$Fe(phen)_3[Sb_2(d\text{-tart})_2] \cdot 8H_2O$; the isomorphous active potassium (ordinary tartar emetic)[46] and ammonium[47] salts, $M_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$; and the racemic potassium salt[48], *dl*-$K_2[Sb_2(tart)_2] \cdot 3H_2O$. Unfortunately, a preliminary report[49], based on an incomplete two-dimensional X-ray structure determination, erroneously stated that the latter compound contained monomeric complex anions with a structure similar to that proposed by Reihlen and Hezel[38].

It is surprising that a dimeric structure with tetranegative tartrate ligands had not been deduced previous to the X-ray structural studies for the antimony(III) tartrate complexes, which have probably been investigated more thoroughly than have any other tartrato complexes. That the formulae of many antimony(III) tartrate salts give the number of water molecules per antimony atom as an odd multiple of one-half induced some early workers to propose a dimeric (though not a tartrato(4-)-bridged) structure for the complex anion present[50]. Moreover, Kahlenberg as early[51] as 1895, and, later, Reihlen and Hezel[38] reported that the freezing point depression of solutions of antimony(III) tartrate salts was inconsistent with a monomeric complex. The latter workers, however, rejected a dimeric structure and concluded that the anomalous colligative properties were the result of simple intermolecular association in the comparatively concentrated solutions studied. They based their conclusion on the known tendencies of carboxylic acids and carboxylates to associate in solution and on their observation that the freezing point depression of antimony(III) tartrate solutions indicated a progressive decline of molecular association with dilution. This concentration dependence of the apparent molecular association has been noted by others[32,52].

Many workers have shown that when ordinary tartar emetic is dried, $1\frac{1}{2}$ moles of water are lost for each mole of antimony present[28,33,34,53]. The residue obtained is water-soluble and crystalline tartar emetic is obtained again upon evaporation of the solution, observations which indicate that no destruction of the complex has occurred to give, for instance, Sb_2O_3. These results indicate that $1\frac{1}{2}$ moles of water of crystallization per antimony are given off when potassium antimony(III) tartrate is dried and agree with the simple formula $KSbC_4H_2O_6 \cdot 1\frac{1}{2}\, H_2O$ (as determined conclusively from the crystal structure determination)[46]. Schmidt[30], in fact, proposed tetradentate coordination of a tartrato(4-) ligand in these antimony(III) complexes. Reihlen and Hezel, however, rejected such a structure as sterically unlikely (for a monomer)[38].

Perhaps an unwillingness on the part of many workers to believe that protons are lost from both the hydroxyl and carboxyl positions of the tartrate ligand in the relatively acidic media in which tartar emetic forms[54] has hindered the acceptance of a quadridentate tartrato(4-) ligand even though ionization of α-hydroxy groups upon coordination at lower pH in other α-hydroxycarboxylatometallate systems has previously been reported[55,56]. It is now irrefutable, however, that tartaric acid can and often does act as a quadridentate tetranegative ligand even under relatively acidic conditions.

(ii) *Structure*

The X-ray structure determinations[44–48] show the geometry of the antimony(III) binuclear tartrato(4-) dinegative complex (Fig. 7) to be strikingly similar to that of the vanadyl(IV) tartrato(4-)-bridged *dd* isomer (Fig. 1). All of the antimony(III) tartrate salts whose structures have been determined contain tartrato(4-)-bridged dimers of the *dd* (or *ll*) type (which are necessarily *trans*) with a four-coordinate, pseudo-trigonal-bipyramidal coordination geometry. The fifth position of the antimony(III) coordination (*i.e.*, the equatorial site occupied by the vanadyl oxygen atom in the analogous vanadyl(IV) compound—Fig. 4). Presumably contains a lone pair of electrons[57]. Precisely such a coordination geometry had pre-

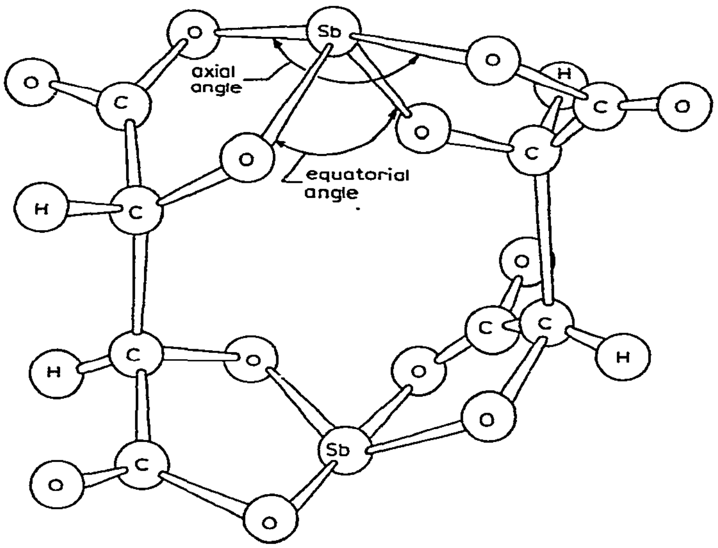


Fig. 7. Geometry of the antimony(III) tartrato(4-)-bridged binuclear complex.

TABLE 2

COORDINATION GEOMETRIES REPORTED FOR TARTRATO(4-)-BRIDGED ANTIMONY(III) DIMERS AND FOR OTHER PSEUDO-TRIGONAL-BIPYRAMIDAL ANTIMONY(III) COMPOUNDS[a]

Compound	*Bond angle*[b]		*Bond length*[b]		*Coordinated atom*	*Ref.*
	Axial	*Equatorial*	*Axial*	*Equatorial*		
Perfect trigonal bipyramid	180	120				
	Tartrato(4-)-bridged dimers					
dl-$(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O^c$	149	98	2.14	2.03	O	44
			2.16	2.04		
l-$Fe(phen)_3[Sb_2(d\text{-tart})_2] \cdot 8H_2O^c$	153(1)	100(1)	2.13(4)	1.93(4)	O	45
			2.16(4)	1.94(4)		
$K_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$						46
Sb_I^d	148	99	2.11	1.97	O	
			2.11	1.99		
Sb_{II}	152	95	2.18	1.98	O	
			2.19	2.01		
$(NH_4)_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O^{c,c}$						47
Sb_1^d	152	96	2.12	1.94	O	
			2.28	2.02		
Sb_2	144	111	1.96	2.05	O	
			2.26	2.07		
dl-$K_2[Sb_2(tart)_2] \cdot 3H_2O^{c,f}$						48
Sb 1[d]	148	93	2.19	2.04	O	
			2.22	2.13		
Sb 2	151	105	2.14	1.89	O	
			2.23	2.10		
Average[g]:	150(2)	100(4)	2.16(5)	2.01(5)		

[continued]

TABLE 2 *(continued)*

Compound	*Bond angle*[b]		*Bond length*[b]		*Coordinated. atom*	*Ref.*
	Axial	*Equatorial*	*Axial*	*Equatorial*		
			Other pseudo-trigonal-bipyramidal complexes			
$SbNbO_4$[h]	150.7(4)	92.1(4)	2.134(9) 2.331(9)	2.008(9) 2.035(9)	O	63
β-Sb_2O_4	148.1(4)	87.9(4)	2.218(9) 2.218(9)	2.032(9) 2.032(9)	O	64
$NaSbF_4$[c,e,i]	148	85	2.08 (10–20) 2.19 (10–20)	1.93(10–20) 2.03(10–20)	F	65
$Sb_4O_5Cl_2$[e,j]	149	97	2.02 2.06	1.89 2.22	O	66
$Sb_4O_5Br_2$[c,e,j]	154	95	2.03 2.07	1.89 2.25	O	66
$CsSb_2F_7$[c,e,k]	135	88	2.02 2.22	2.08 2.37	F	67
$SbOCl$[c,e,j]	138	80	2.11(30) 2.18(30)	2.00(30) 2.18(30)	O	68
$Sb_8O_{10}(OH)_2I_2$[e,l]						69
Sb_1[d]	145	103	2.17 2.17	2.03 2.20	O	
Sb_2	145	80	2.17 2.17	2.04 2.24	O	
Sb_3	145	100	2.17 2.17	2.03 2.24	O	
Sb_4	145	101	2.17 2.17	2.02 2.22	O	
$[Sb_8O_8(OH)_4]$-$[(OH)_{2-x}(H_2O)_{1+x}]Cl^{e}_{2+x}$	143	85	2.15(30) 2.15(30)	2.04(30) 2.17(30)	O	70
$(C_5H_5NH)\ [SbCl_4]$[m]		94	2.63 2.63	2.38 2.38	Cl	71
$H[Sb(C_2H_2O_2S)_2]$[n]	157.6	97.5	2.26(2) 2.30(2)	2.426(8) 2.431(8)	O, S	72
$SbCl_3 \cdot C_6H_5NH_2$[p]	194(2)	96.1(6)	2.52(4) 2.54(2)	2.32(1) 2.34(2)	Cl,N	138
Average[o]:	147(4)	92(7)	2.16(5)	2.09(10)		

[a] See Fig. 7 for definition of axial and equatorial parameters. [b] Bond angles are in degrees and lengths, in Angstroms. Where known, the e.s.d. of the last figure is in parentheses. [c] Bonding parameters were calculated from the reported atomic positions. [d] The nomenclature in the original paper was used for these crystallographically nonequivalent antimony atoms. [e] Positions of the light atoms are very uncertain. [f] Partially refined structure. [g] Unweighted average over all antimony sites with mean absolute deviation of the last figure in parentheses. [h] An additional oxygen atom lies at 2.58 Å from the antimony atom. [i] The antimony atom has a fivefold coordination if a fluorine atom at 2.5 Å is included. [j] Other, crystallographically nonequivalent antimony(III) atoms, which do not exhibit a pseudo-trigonal-bipyramidal fourfold coordination, are present. [k] The fluorine atom positions are questioned in a later paper[73]. [l] The isomorphous bromine compound exhibits very similar bond parameters. [m] Pyridinium tetrachloroantimonate(III). The antimony atom is reported as hexacoordinate, but if two chlorine atoms at 3.12 Å are neglected, the geometry is pseudo-trigonal-bipyramidal. [n] Hydrogen bis(thioglycollato(2-))-antimonate(III). Oxygen atoms occupy the axial positions and sulfur atoms, the equatorial positions. [o] Unweighted average for bonds involving oxygen coordination with mean absolute deviation of the last figure in parentheses. [p] Antimony trichloride - aniline acceptor-donor complex. The nitrogen atom is axial.

viously been predicted (for a monomer)[58]. Both the axial and equatorial angles of the antimony(III) tartrate complex anions are depressed from the respective values of 180 and 120 deg., which are required for an ideal trigonal bipyramid. This depression can be explained in terms of the relative magnitudes of the lone pair–bonding pair and bonding pair–bonding pair repulsions[59].

A pseudo-trigonal-bipyramidal fourfold coordination for trivalent antimony was first described by Edstrand[60] for several antimony(III) oxyhalides and has since been reported for a large number of antimony(III) compounds[61]. Table 2 contains a compilation of pertinent axial and equatorial dimensions (refer to Fig. 7) determined by X-ray studies. Some of these results are inaccurate as the positions of the lighter atoms in some of the structure determinations (mainly the earlier ones) were not fully refined. Moreover, some of the results presented are for highly ionic or bonded crystals (specifically those containing oxide or halide anions) and there may be some doubt as to the validity of comparing their geometries with the other cases. Attempts have been made, however, to select those structures where there appears to be a definite fourfold pseudo-trigonal-bipyramidal coordination. It is interesting to note that, with the possible exception of $PbSbO_2Cl$ —which has been reported as four-coordinate, square-pyramidal[62], but whose structure determination has been seriously challenged[61]—,all antimony(III) compounds studied to date by X-ray diffraction techniques exhibit a coordination geometry which may be described as approximating a trigonal bipyramid when there is a definite fourfold coordination and a decet of electrons about the antimony atoms.

We see that the geometry about the antimony atom in the tartrato(4-)-bridged dimers is quite similar to that found in other four-coordinate antimony(III) compounds. As does the vanadyl(IV) *dd* dimer (Table 1), the antimony(III) tartrato(4-) anions exhibit hydroxyl oxygen–metal (equatorial) bond lengths which are significantly shorter than the carboxyl oxygen–metal (axial) bond lengths. This axial–equatorial bond length difference is a usual feature of trigonal-bipyramidal molecular geometries[74] and has been explained by electron-pair-repulsion arguments[75]; also, we note that there cannot be five equivalent sp^3d hybrid orbitals of the antimony(III) atom. Hydrogen bis(thioglycollato(2-))antimonate(III)[72], about which more will be said later, presents a clearly-established case where the equatorial bond length is longer than the axial (Table 2) and might appear to contradict the statement that axial bonds are "always longer" than equatorial bonds in trigonal-bipyramidal-type molecules[76]; in this specific case, however, the axial and equatorial ligands are not identical. The larger size of the equatorial atoms (sulfur) relative to the axial atoms (oxygen) favors formation of a longer equatorial bond; this apparently reverses the usual bond length ordering.

To date, we have found only one report[77] of structures of coordination compounds containing α-hydroxycarboxylate ligands with the α-hydroxy group both unionized and coordinated. In *trans*-bis(glycollato)copper(II) and in *trans*-

aquobis(*d,l*-lactato)copper(II) hemihydrate, the hydroxyl oxygen–metal distances (1.93–1.97 Å) are slightly longer than the carboxyl oxygen–metal distances (1.91–1.93 Å), while in diaquobis(2-hydroxy-2-methylpropionato)copper(II), the corresponding values[77] are 2.01 and 1.89 Å. This bond length ordering is just the opposite of that observed in the vanadyl(IV) and antimony(III) α-hydroxycarboxylates, in which the α-hydroxy groups are ionized (Tables 1 and 2). This fact indicates, as one might expect, that an ionized α-hydroxy group coordinates more strongly than an unionized one. It is interesting to note that in the corresponding complexes where the hydroxyl hydrogen has been replaced by alkyl or aryl groups, the difference between the α-oxygen–metal and carboxyl oxygen–metal distances (respectively, 2.1–2.5 Å and about 1.94 Å) is still larger[77]. This observation might indicate a lower basicity for –OR and –OAr groups than for –OH groups (see, however, ref. 78).

Although a *dd*-type tartrato(4-)-bridged dimer will possess D_2 symmetry with three mutually perpendicular twofold rotation axes when all chemically equivalent bond lengths and bond angles are equal (Fig. 1 and 7), only two of the five antimony(III) tartrate structures which have been solved contain anionic complexes with any crystallographic symmetry at all. All of these complexes, however, do *approximate* D_2 symmetry. The binuclear complex of the racemic ammonium salt[44] possesses a crystallographic twofold axis passing between the tartrato(4-) chains, equidistant from them, and perpendicular to the antimony–antimony vector. This symmetry element provides two crystallographically equivalent tartrato(4-) ligands in each dimer. The *l*-tris(1,10-phenanthroline)iron(II) compound[45] contains anions in which a crystallographic twofold axis passes through the central carbon–carbon bonds of the bridging groups giving two crystallographically nonequivalent tartrate groups (each with C_2 symmetry) in each binuclear anion. Thus the symmetry of the complex is the same as that of the active dimer in ammonium vanadyl(IV) tartrate[22].

(iii) *Isomer stabilities*

In contrast to the vanadyl(IV) tartrate system, neither of the racemic antimony(III) tartrate salts whose structures have been determined contains *dl*-type dimers. Crystals of both *dl*-$(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O$[44] and *dl*-$K_2[Sb_2(tart)_2] \cdot 3H_2O$[48] consist of a racemic mixture of *dd* and *ll* isomers. *E.g.*, the latter compound should actually be formulated as $K_4[Sb_2(d\text{-tart})_2]\ [Sb_2(l\text{-tart})_2] \cdot 6H_2O$. The case of $Na_4[(VO)_2(d\text{-tart})\ (l\text{-tart})] \cdot 12H_2O$[23] has to date provided the only structural data for a *dl*-type tartrato(4-)-bridged dimer. However, N. D. Chasteen in these laboratories has isolated crystalline $Na_4Cu_2(d\text{-tart})(l\text{-tart}) \cdot 10H_2O$ and shown its dimeric nature by e.p.r. techniques (to be published).

The absence of a *dl* binuclear species in the two racemic antimony(III) tartrate salts whose structures have been determined provides weak evidence that the racemic antimony(III) dimeric isomer is unstable with respect to disproportionation to the active isomers. Moreover, a *meso*-tartrate-containing complex of antimony(III) is apparently also unstable[38]. We have already noted the apparent absence of a vanadyl(IV) *meso*-tartrate species.

(iv) *Intermetallic distances in the tartrato(4-)-bridged dimers*

The data in Tables 1 and 2 show that the equatorial angles are larger (*i.e.*, the hydroxyl oxygen atoms are depressed less) in the active vanadyl(IV) tartrato(4-)-bridged dimer than in the corresponding antimony(III) complexes. The vanadyl(IV) *dd* dimer better approximates a trigonal-bipyramidal coordination geometry than does the antimony(III) tartrato(4-) species. The differences in the depressions of the hydroxyl groups for the various tartrato(4-)-bridged complexes probably account to a large extent for the observed increase in the metal–metal distances within these dimers: vanadyl(IV) *dl* < vanadyl(IV) *dd* < antimony(III) *dd* (Table 3). In the absence of distortion from a square-pyramidal coordination geometry for the vanadyl(IV) *dd* complex, one would expect this binuclear species to have a smaller metal–metal distance than the *dl* isomer since, as we have already pointed out, the vanadyl groups are staggered in the latter isomer but are opposed (and ideally collinear) in the former. It has been proposed[28] that the greater metal–metal distance in the active vanadyl(IV) tartrato(4-) complex causes its e.p.r. spectrum to differ from that of the racemic isomer—in which electron exchange between the vanadium atoms occurs to a significant extent[20,79]—in part by modifying the zero-field splitting. Subsequent measurements of e.p.r. spectra of frozen solutions and single crystals showed that the two isomers differ more in the orientation than in the magnitude of their zero-field splitting tensors[80].

TABLE 3

METAL–METAL DISTANCES IN THE TARTRATO(4-)-BRIDGED DIMERS

Compound	*Metal–metal distance*[a]	*Ref.*
	Vanadyl(IV) complexes	
$(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$	4.352(7)	22
$Na_4[(VO)_2(d\text{-tart})(l\text{-tart})] \cdot 12H_2O$	4.082(2)	23
	Antimony(III) complexes	
$dl\text{-}(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O$	5.22	44
$l\text{-Fe(phen)}_3[Sb_2(d\text{-tart})_2] \cdot 8H_2O$	5.025(2)	45
$K_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$	5.05	46
$(NH_4)_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$	5.13	47
$dl\text{-}K_2[Sb_2(tart)_2] \cdot 3H_2O$[b]	5.18	48
Average for Sb^{III} *dimers*[c]:	5.12(7)	

[a] All distances (in Ångstroms) were calculated from the reported atomic positions. Where known, the e.s.d. of the last figure is in parentheses. [b] Partially refined structure. [c] Unweighted average with mean absolute deviation of the last figure in parentheses.

D. GEOMETRIES OF COORDINATED AND UNCOORDINATED TARTRATE GROUPS

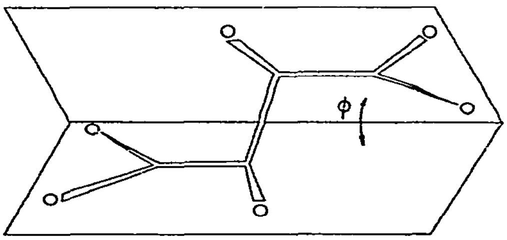
(i) *Introduction*

There have been many X-ray structure reports of the various forms of tartaric acid—active, racemic, and *meso* (Fig. 5)—and their salts; however, the only crystal structure studies of compounds containing coordinated tartrate ligands, excluding some of the alkali metal and alkaline earth tartrates which involve electrostatic coordination to the cation (*e.g.*, strontium and calcium tartrates[141]), are those of the tartrato(4-)-bridged dimers. The abundance of structural data for compounds containing uncoordinated tartrate groups provides an ideal opportunity for comparing the geometries and conformations of the tartrato(4-) ligands with those of free tartrate groups. We will see that such a comparison will prove fruitful in our discussion of the relative stabilities and coordination geometries of the binuclear tartrato(4-) complexes.

It should perhaps be pointed out at this time—before discussing the geometries of the various tartrate isomers—that there is considerable disagreement concerning the naming of the two enantiomers of tartaric acid[82]. Throughout this review, we will designate the "natural", dextrorotatory isomer, whose absolute configuration has been determined[83,84] and is illustrated in Fig. 5, as the *d* form.

(ii) *Planar features of tartrate groups and chelation*

An apparently generic feature of α-hydroxycarboxylates is the approximate coplanarity of the carboxyl group, adjacent central carbon atom, and α-hydroxyl oxygen atom[85]. This coplanarity allows all of the non-hydrogen atoms of both active and *meso*-tartrate groups to be described as lying in two planes (Figs. 8 and 9)—the one containing the two carboxyl oxygen atoms, the α-hydroxyl oxygen atom, and the two carbon atoms at one end of the tartrate group, the other containing the corresponding atoms at the other end. Table 4 gives the average deviations of the five non-hydrogen atoms from their best least-squares planes as defined in Figures 8 and 9, and of the four carbon atoms from their best planes, as



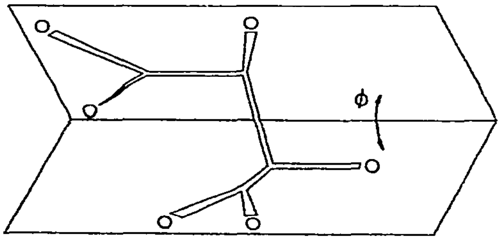


Fig. 8. Configuration of the *d*-tartrate group in the solid state.

Fig. 9. Configuration of the *meso*-tartrate group in the solid state.

TABLE 4

GEOMETRICAL PARAMETERS ILLUSTRATING PLANAR FEATURES OF TARTRATE GROUPS

Compound	*Deviations of atoms from best planes*[a]			*Angles between best planes*[b]			*α-Hydroxyl to adjacent carboxyl oxygen distances*		*Ref.*
	plane 1	*plane 2*	*plane 3*	*1–3*	*2–3*	*1–2*	*Atoms*[c]	*Distance*[d]	
				Tartrato(4-)-bridged dimers					
				Vanadyl(IV)					
$(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$									22
tart 1[e]	.10(.03)	.10(.03)	.32	44	44	61	O(2)–O(4)	2.57(2)[f]	
tart 2	.08(.04)	.08(.04)	.47	47	47	61	O(5)–O(7)	2.55(2)	
$Na_4[(VO)_2(d\text{-tart})(l\text{-tart})] \cdot 12H_2O$	.07(.42)	.01(.29)	.02	68	63	49	O(3)–O(5)	2.58(1)[f]	23
							O(4)–O(6)	2.54(1)	
				Antimony(III)					
$dl\text{-}(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O$	.05(.26)	.03(.06)	.06	51	57	73	O(1)–O(3)	2.68[f]	44
							O(6)–O(4)	2.66	
$l\text{-}Fe(phen)_3[Sb_2(d\text{-tart})_2] \cdot 8H_2O$									45
tart 1[e]	.01(.08)	.01(.08)	.60	60	60	71	O2Tar1–O3Tar1	2.59(4)[f]	
tart 2	.00(.15)	.00(.15)	.36	43	44	65	O2Tar2–O3Tar2	2.60(5)	
$K_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$									46
tart 1[e]	.15(.72)	.09(.13)	.01	74	56	50	OI-1–OI-5	2.80[f]	
							OI-3–OI-6	2.71	
tart 2	.03(.30)	.02(.09)	.04	58	51	71	OII-1–OII-5	2.91	
							OII-3–OII-6	2.52	
$(NH_4)_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$[h]									47
tart 1[e]	.09(.41)	.19(.02)	.08	89	31	62	O(12)–O(10)	2.79[f]	
							O(7)–O(9)	2.44	
tart 2	.12(.42)	.05(.28)	.13	59	65	57	O(1)–O(3)	2.80	
							O(6)–O(4)	2.62	
$dl\text{-}K_2[Sb_2(tart)_2] \cdot 3H_2O$[i]									48
tart 1[e]	.05(.03)	.05(.31)	.23	90	28	69	O(1)–O(5)	2.73[f]	
							O(13)–O(4)	2.79	
tart 2	.06(.20)	.01(.06)	.27	17	89	75	O(6)–O(7)	2.74	
							O(10)–O(11)	2.69	
Average for Sb compounds[j]:				60(16)	53(13)	66(7)		2.69(9)	

[continued]

TABLE 4 *(continued)*

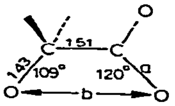
Compound	*Deviations of atoms from best planes*[a]			*Angles between best planes*[b]			*α-Hydroxyl to adjacent carboxyl oxygen distances*		*Ref.*
	plane 1	*plane 2*	*plane 3*	*1–3*	*2–3*	*1–2*	*Atoms*[c]	*Distance*[d]	
				Tartaric acids and salts					
				Compounds with active tartrate groups					
Tartaric acids[k]									
d-$C_4H_6O_6$	.02	.03	.03	64	60	56[l]	O(3)–O(1) O(6)–O(4)	2.655(5) 2.752(6)	86
dl-$C_4H_6O_6 \cdot H_2O$[m]	.05	.09	.00	61	50	69	O(2)–O(3) O(5)–O(4)	2.68[f] 2.69	87
Average for acids[j]:				62(2)	55(5)	62(7)		2.69(2)	
Bitartrate salts[n]									
NH_4 H *d*-$C_4H_4O_6$	.04	.02	.01	64	53	62	O(2)–O(3) O(6)–O(4)	2.71[f] 2.69	88
Rb H *d*-$C_4H_4O_6$[o]	.04	.04	.01	63	55	63	O(2)–O(3) O(6)–O(4)	2.73[f] 2.66	89
NH_4 H *dl*-$C_4H_4O_6$[p]	.03	.02	.01	65	52	63	O(2)–O(3) O(6)–O(4)	2.79[f] 2.72	90
Average for bitartrates[j]:				64(1)	53(1)	63(0)		2.72(3)	
Divalent tartrate salts									
Li NH_4 *d*-$C_4H_4O_6 \cdot H_2O$	.01	.05	.07	55	71	54	O(2)–O(3) O(5)–O(4)	2.61[f] 2.62	91
Na K *d*-$C_4H_4O_6 \cdot 4H_2O$[q]	.03	.09	.01	61[r]	68[r]	51	O(2)–O(5) O(3)–O(6)	2.70[f] 2.67	92
Na K *dl*-$C_4H_4O_6 \cdot 4H_2O$	.12	.09	.00	56	72	54	O(2)–OH(5) O(3)–OH(6)	2.78[f] 2.80	93
Li NH_4 *dl*-$C_4H_4O_6 \cdot H_2O$[s]	.02	.06	.01	52	61	67	O(2)–O(3) O(5)–O(4)	2.65 (2) 2.59 (3)	90
Na_2 *d*-$C_4H_4O_6 \cdot 2H_2O$[t]	.04[.04]	.10[.07]	.02[.02]	64[65]	64[70]	52[45]	O(1)–O(3) O(6)–O(4)	2.60 2.71	140
Sr *d*-$C_4H_4O_6 \cdot 3H_2O$[t]	.04[.04]	.05[.06]	.18[.06]	86[64]	43[70]	44[47]	O(1)–O(3) O(6)–O(4)	2.70 2.65	141
Ca *d*-$C_4H_4O_6 \cdot 4H_2O$[t]	.12[.12]	.01[.01]	.01[.01]	36[37]	54	89	O(1)–O(3) O(6)–O(4)	2.61 2.65	141
Average for divalent tartrate salts[j,u]:				58(5)	65(5)	54(5)			
				Compounds with meso-tartrate groups[v]					
Tartaric acids[k]									
meso-$C_4H_6O_6 \cdot H_2O$ (triclinic)	.02	.03				59	O(1)–O(3) O(6)–O(4)	2.64[f] 2.63	94

Compound	*Deviations of atoms from best planes*[a]			*Angles between best planes*[b]			*α-Hydroxyl to adjacent carboxyl oxygen distances*		
	plane 1	*plane 2*	*plane 3*	*1–3*	*2–3*	*1–2*	*Atoms*[c]	*Distance*[d]	*Ref.*
meso-$C_4H_6O_6 \cdot H_2O$ (monoclinic)	.04	.04				47	O(1)–O(3)	2.57[f,w]	94
							O(6)–O(4)	2.65	
meso-$C_4H_6O_6$ (triclinic)	.04	.05				69	O(1)–O(3)	2.60[f]	94
							O(6)–O(4)	2.68	
Average for acids[j]:						58(8)		2.63(3)	
Divalent tartrate salts									
K_2 *meso*-$C_4H_4O_6 \cdot 2H_2O$[x]	.05	.03				56[y]	O(1)–O(3)	2.75[f]	95
							O(6)–O(4)	2.68	
Rb_2 *meso*-$C_4H_4O_6 \cdot 2H_2O$	.03	.03				61	O(1)–O(3)	2.63[f]	95
							O(6)–O(4)	2.67	
Average for divalent tartrate salts[j]:						58(2)		2.68(3)	

[a] Absolute deviation (distance to plane in Ångstroms) averaged over all the atoms used in calculating the best plane. The distance of the coordinated metal atom to the plane in the tartrato(4-)-bridged dimers is given in parentheses. Planes 1 and 2 are the best least-squares planes containing the carboxyl group and adjacent central carbon atom-α-hydroxyl group at the two ends of the tartrate chain (see text). Plane 3 is the best plane for the four-carbon tartrate chain. Except where noted, we calculated these best planes from the reported atomic coordinates. [b] In degrees. The angle between planes 1 and 2 corresponds to ϕ in Figures 8 and 9. [c] Atom designations in the original paper. The first atom listed is the carboxyl oxygen atom; the second atom is the α-hydroxyl oxygen atom. [d] The distances given (in Ångstroms) are those reported in the original paper except where noted. The e.s.d. of the last figure, where known, is in parentheses. [e] There are two crystallographically non-equivalent tartrate groups present. [f] Calculated from the reported atomic positions. [h] The atomic coordinates reported for this compound[47] appear to be highly inaccurate. [i] Partially refined structure. [j] Unweighted average with mean absolute deviation in parentheses. [k] The shortest α-hydroxyl to adjacent carboxyl oxygen distances for unionized tartaric acids all involve the unprotonated carboxyl oxygen atom except in the case of monoclinic *meso*-tartaric acid monohydrate. [l] Reported as 54.6 deg. in the original paper[86]. [m] The atomic coordinates reported in *Structure Reports for 1951*[96] were used in the calculations as the atomic coordinates were not given in the original paper[87]. [n] Bitartrate is defined as a monovalent acid tartrate. Plane 1 includes the protonated carboxyl group (where known) and plane 2, the ionized carboxyl group. The upper figure in each set of α-hydroxyl to adjacent carboxyl oxygen distances is for a contact with the unprotonated carboxyl oxygen of the unionized carboxyl group. [o] The z coordinate of O(4), reported in the original paper as 0.496 fractional cell units[89], is obviously in error. A z coordinate of 0.388 was taken from data for the isomorphous ammonium salt[88] and was used in the calculations. [p] There is no indication as to which carboxyl oxygen atom is protonated. [q] The accuracy of this structure is low. [r] Reported as 60 ± 2 deg. in the original paper[92]. [s] That some of the reported bonding parameters involving atoms C(2) and C(3) of this structure could not be reproduced using the reported atomic positions[90] indicates an error in the coordinates given for one or both of these atoms. The calculations were therefore carried out on a new set of atom positions obtained by a least-squares refinement of the original data (A. J. J. Sprenkels, private communication). [t] The deviations of atoms from best planes given in brackets are those reported by Ambady[81]. The interplanar angles given in brackets are those which we calculate from these reported best planes. The y coordinates of C(3) and O(4) reported as 0.6787 and 0.5340 for strontium tartrate trihydrate[141] are in error. Corrected values of 0.6687 and 0.6340 were used in these calculations (G. K. Ambady, private communication). [u] The angles involving plane 1 of the calcium tartrate tetrahydrate structure and plane 3 of the strontium tartrate trihydrate structure were not included in these averages owing to rather significant deviations from planarity. Ambady attributes the distortion of the tartrate ion in the former structure to hydrogen and ionic bonding forces.[141] [v] The carbon atoms of the *meso*-tartrate groups are nonplanar owing to the conformation of the carbon chain in this isomer. Accordingly, no data for plane 3 have been reported. [w] This distance involves a protonated carboxyl oxygen, O(1). The monoclinic-monohydrate form of *meso*-tartaric acid is the only tartrate compound known to have a protonated carboxyl oxygen adjacent to the α-hydroxyl oxygen. [x] The x coordinates of O(1) and O(4), which are reported as 0.8852 and 0.8534 fractional cell units, are in error[97]. Corrected values of 0.8552 and 0.8354 were used in these calculations. [y] Reported as 57 deg[95].

determined from X-ray structure data for both coordinated and uncoordinated tartrate groups. In addition, this Table also lists the interplanar angles and the distances between the α-hydroxyl atoms and adjacent carboxyl oxygen atoms.

One sees that in tartrate groups, whether coordinated or uncoordinated and whether ionized or unionized, the five non-hydrogen atoms at one end of the residue do, indeed, exhibit an approximate coplanarity. This planarity is indicated also by the close contacts between the α-hydroxyl oxygen and adjacent carboxyl oxygen atoms. The values found for this contact lie very close to the distance of 2.60 Å (2.62, 2.64) calculated for a perfectly planar group in which the carboxyl oxygen atom–carbon atom bond adjacent to the α-hydroxyl group has a bond order of 2 ($1\frac{1}{2}$, 1). Standard bond lengths[98] and bond angles, which for this purpose are sufficiently close to those observed for tartrate groups, were used for the calculation (the angle given as 120° in the following diagram is usually slightly

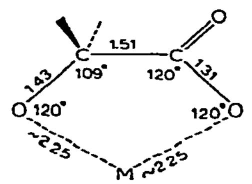


	a	b
$\mathrm{C=O}$	1.23	2.60
$\mathrm{C}\mathrel{\overset{\cdots}{-}}\mathrm{O}$	1.26	2.62
$\mathrm{C-O}$	1.31	2.64

smaller). If the carboxyl group were rotated 90 deg. about the C(sp^3)-C(sp^2) bond from the planar eclipsed position, the distance (b) between the α-hydroxyl and carboxyl oxygen atom would increase to about 3.1 Å.

Intramolecular electrostatic attractions between the α-hydroxyl and adjacent carboxyl oxygen atoms in the solid state[99] and Pauling's bent-bond conception of the double bond[85] have been proposed to explain the eclipsing of the α-hydroxyl oxygen atom by the carboxyl group. Calculations[81] indicate that a minimum in the intramolecular contact potential energy curve for rotation about the C(sp^2)-C(sp^3) bond in tartrates occurs at a position close to the eclipsed conformation observed. Hydrogen bonding[85,99] and intermolecular forces in the crystalline state[85] are apparently not the determining factors for the short α-hydroxyl to adjacent carboxyl oxygen atom contacts. Chelation, as observed in the tartrato(4-)-bridged dimers and in the alkaline earth tartrates[141], may, in some cases, aid in maintaining a planar geometry. It is interesting to note that in the absence of an α-hydroxy substituent, the C_α-C_β bond eclipses the C=O of the carboxyl group[85,136].

The coplanarity of the carboxyl and α-hydroxyl groups in α-hydroxycarboxylates provides an ideal geometry for chelation such as that observed in the tartrato(4-)-bridged dimers. Using standard bond lengths[98] and bond angles, and assuming sp^2 hybridization of the coordinating oxygen atoms (as indicated by the angles observed about the coordinated oxygen atoms in the vanadyl(IV) and antimony(III) α-hydroxycarboxylates), we calculate an "ideal" oxygen to metal distance of about 2.25 Å for an α-hydroxycarboxylate chelate:



This distance can be compared with the average coordination distances of about 1.95 Å and 2.08 Å observed, respectively, for vanadyl(IV) α-hydroxycarboxylates and antimony(III) tartrates (Tables 1 and 2). The slightly shorter than "expected" coordination distances observed result in part from the slightly smaller than 120 deg. angles found about the carboxyl carbon and the nominally sp^2 coordinated oxygen atoms (the average C-O-M angle for the vanadyl(IV) α-hydroxycarboxylates[22,23,26] is 116 deg.; the average for the antimony(III) tartrates[44–48] is 114 deg.) and from the deviations of the coordinated metal atoms from the best planes of the ligands (Table 4). It would be interesting to determine whether the stabilities of α-hydroxycarboxylate complexes can be related to the metal ion–coordinated oxygen atom distance needed to maintain the approximate planarity and normal bonding parameters of the chelating ligand. Thus, one might expect that for metal ions giving metal atom–oxygen atom coordination distances above and below some certain range, there would be a decrease in stability of α-hydroxycarboxylate complexes owing to distortion of the chelating ligand. Small distortions in the ligand, however, can undoubtedly give a relatively wide range of acceptable coordination distances. Chelation of tartrate groups with Ca^{2+} and Sr^{2+} ions results in much longer coordination distances (about 2.5 and 2.6 Å[141]) than in the vanadyl(IV) and antimony(III) compounds.

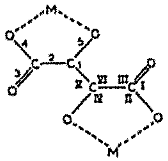
(iii) *Interatomic distances and bond angles in coordinated and uncoordinated tartrate groups*

Tables 5 and 6 present the tartrate group bonding parameters as determined by X-ray structural studies. These data are given, not only to facilitate comparisons between the geometries of uncoordinated tartrate groups and those of the ligands in the tartrato(4-)-bridged dimers, but also to provide a complete compilation of the structure parameters determined to date for tartrate compounds. Several of these tartrate structures have been reported in sources which are not readily available; moreover, in many cases, only the atomic coordinates were given.

Tables 5 and 6 show that the bonding parameters of uncoordinated and coordinated tartrate groups are very similar. The carbon atom–α-hydroxyl oxygen atom and the carbon atom—coordinated carboxyl oxygen atom distances in the tartrato(4-)-bridged complexes (respective averages, 1.43 and 1.31 Å) are those expected for single bonds[98] and are very close to those found for the corresponding carbon atom—protonated oxygen atom distances in the free tartrates. Thus,

TABLE 5

LIGAND BOND LENGTHS AND BOND ANGLES IN TARTRATO(4-)-BRIDGED DIMERS



Compound	*Bond lengths*[a]					*Bond angles*[a]						*Ref.*
	1	*2*	*3*	*4*	*5*	*I*	*II*	*III*	*IV*	*V*	*VI*	
				Vanadyl(IV)								
$(NH_4)_4[(VO)_2(d\text{-tart})_2]\cdot 2H_2O$												22
tart 1[b]	1.49(3)	1.45(3)	1.22(4)	1.28(4)	1.46(3)	122(1–2)	118(1–2)	115(1–2)	110(1–2)	103(1–2)	120(1–2)	
tart 2	1.54(4)	1.51(3)	1.37(3)	1.35(3)	1.41(3)	115(1–2)	118(1–2)	124(1–2)	100(1–2)	94(1–2)	119(1–2)	
$Na_4[(VO)_2(d\text{-tart})(l\text{-tart})]\cdot 12H_2O$	1.553(11)	1.523(11)	1.227(10)	1.277(10)	1.407(10)	124.1(6)	113.9(5)	120.8(6)	109.9(7)	108.5(6)	107.0(4)	23
		1.534(11)	1.229(9)	1.312(9)	1.410(9)	125.3(4)	114.5(5)	121.2(6)	110.6(7)	109.5(7)	107.5(4)	
				Antimony(III)								
dl-$(NH_4)_2[Sb_2(\text{tart})_2]\cdot 4H_2O$[c]	1.46	1.43	1.17	1.29	1.46	117	112	116	108	108	110	44
		1.53	1.29	1.42	1.47	123	120	130	118	109	115	
l-$Fe(\text{phen})_3[Sb_2(d\text{-tart})_2]\cdot 8H_2O$[c,d]												45
tart 1[b]	1.49	1.56	1.19	1.28	1.38	126	115	119	111	114	105	
tart 2	1.55	1.52	1.25	1.25	1.41	124	119	117	109	111	108	
$K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$[c]												46
tart 1[b]	1.54	1.54	1.17	1.19	1.36	124	117	114	113	106	108	
		1.57	1.30	1.25	1.39	126	120	115	119	115	114	
tart 2	1.53	1.53	1.22	1.20	1.40	120	109	115	114	99	109	
		1.56	1.27	1.30	1.42	127	119	131	122	116	110	
$(NH_4)_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$[c,e]												47
tart 1[b]	1.63	1.70	0.65	1.32	1.44	113	61	115	93	87	87	
		2.08	1.26	1.91	1.77	125	130	121	140	133	92	
tart 2	1.78	1.36	1.08	1.31	1.36	100	109	109	103	95	105	
		1.44	1.40	1.44	1.55	124	127	127	124	105	112	
dl-$K_2[Sb_2(\text{tart})_2]\cdot 3H_2O$[c,f]												48
tart 1[b]	1.55	1.49	1.15	1.38	1.42	117	114	117	117	104	105	
		1.54	1.33	1.44	1.47	129	114	128	118	108	113	
tart 2	1.43	1.46	1.27	1.29	1.44	113	120	120	109	109	109	
		1.51	1.33	1.38	1.51	119	122	125	114	113	113	
Average[g]:	1.51(4)	1.52(3)	1.25(5)	1.31(6)	1.43(3)	122(4)	117(3)	120(4)	113(4)	108(4)	111(4)	

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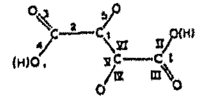
[a] Bond lengths are in Ångstroms and angles, in degrees. Where known, the e.s.d. of the last figure is in parentheses. [b] There are two crystallographically nonequivalent tartrate groups present. [c] The bonding parameters were calculated from the reported atomic positions. [d] The maximum e.s.d. in bond lengths is about 0.05 Å and that in the bond angles is about 2 deg[45]. [e] The structure parameters for this compound appear to be very inaccurate. [f] Partially refined

TABLE 6

BOND LENGTHS AND BOND ANGLES OF TARTARIC ACID AND NORMAL TARTRATE SALTS



Compound	Bond lengths[a]					Bond angles[a]						Ref.
	1	2	3	4	5	I	II	III	IV	V	VI	
Compounds with active tartrate groups												
Tartaric acids												
$d\text{-}C_4H_6O_6$	1.542(7)	1.519(7)	1.198(7)	1.315(6)	1.400(6)	125.5	108.9	123.6	108.4	111.1	106.8	86
		1.527(7)	1.202(6)	1.319(7)	1.408(6)	125.9	110.9	125.2	111.8	111.4	110.5	
$dl\text{-}C_4H_6O_6 \cdot H_2O$[b]	1.53	1.44	1.20	1.28	1.36	120	113	120	110	108	110	87
		1.52	1.22	1.33	1.49	124	116	123	112	110	110	
Average for acids[c]:	1.54(1)	1.50(3)	1.20(1)	1.31(2)	1.41(4)	124(2)	112(2)	123(2)	111(2)	110(1)	109(1)	
Bitartrate salts[d]												
$NH_4\ H\ d\text{-}C_4H_4O_6$	1.528	1.524	1.220	1.311	1.415	124.5	112.5	123.1	110.5	110.4	108.9	88
		1.531	1.263[e]	1.261[e]	1.416	124.8[e]	117.0[e]	118.2[e]	113.0	111.5	109.5	
$Rb\ H\ d\text{-}C_4H_4O_6$[f,g]	1.56	1.52	1.20	1.22	1.44	130	108	123	112	109	109	89
		1.56	1.20[e]	1.23[e]	1.46	132[e]	112[e]	116[e]	113	110	110	
$NH_4\ H\ dl\text{-}C_4H_4O_6$[h]	1.52	1.55	1.21	1.26	1.48	126	108	115	108	108	112	90
		1.56	1.24	1.27	1.50	126	119	126	113	110	114	
Average for bitartrates[c]:	1.54(2)	1.54(2)			1.45(3)				112(2)	110(2)	111(2)	
Divalent tartrate salts[d]												
$Li\ NH_4\ d\text{-}C_4H_4O_6 \cdot H_2O$	1.52	1.51	1.26	1.26	1.41	123	117	117	108	110	111	91
		1.52	1.29	1.28	1.43	124	119	120	111	112	111	
$Na\ K\ d\text{-}C_4H_4O_6 \cdot 4H_2O$[i]	1.53	1.52	1.15	1.22	1.40	128	115	114	112	106	110	92
		1.58	1.32	1.36	1.51	129	117	115	115	113	118	
$Na\ K\ dl\text{-}C_4H_4O_6 \cdot 4H_2O$	1.53	1.58	1.19	1.28	1.40	124	111	114	111	108	113	93
		1.58	1.28	1.29	1.40	125	118	123	117	122	114	
$Li\ NH_4\ dl\text{-}C_4H_4O_6 \cdot H_2O$	1.52	1.52	1.25	1.28	1.46	124	117	115	107	105	106	90
		1.53	1.26	1.28	1.47	125	120	118	111	106	107	

[continued]

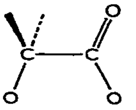
TABLE 6 *(continued)*

Compound	*Bond lengths*[a]					*Bond angles*[a]						*Ref.*
	1	*2*	*3*	*4*	*5*	*I*	*II*	*III*	*IV*	*V*	*VI*	
Na$_2$ *d*-$C_4H_4O_6 \cdot 2H_2O$	1.533(4)	1.526(4)	1.240(4)	1.248(4)	1.414(4)	125.7(3)	115.5(3)	116.9(3)	110.0(3)	109.5(3)	107.2(3)	140
		1.540(4)	1.251(4)	1.249(4)	1.420(4)	127.5(3)	115.8(3)	118.3(3)	113.0(3)	111.6(3)	110.5(3)	
Sr *d*-$C_4H_4O_6 \cdot 3H_2O$	1.54(3)	1.54(3)	1.23(3)	1.25(3)	1.42(3)	124(2)	113(2)	116(2)	108(2)	110(2)	108(2)	141
		1.56(3)	1.27(3)	1.27(3)	1.45(3)	125(2)	120(2)	121(2)	110(2)	113(2)	108(2)	
Ca *d*-$C_4H_4O_6 \cdot 4H_2O$	1.52(1)	1.50(1)	1.27(1)	1.24(1)	1.43(1)	123(1)	118(1)	116(1)	110(1)	111(1)	110(1)	141
		1.50(1)	1.31(1)	1.26(1)	1.44(1)	124(1)	122(1)	118(1)	112(1)	112(1)	115(1)	
Average for divalent tartrate salts[c,j]:	1.53(1)	1.53(2)	1.26(2)	1.27(2)	1.43(2)	125(1)	117(2)	118(2)	111(2)	111(3)	110(2)	
Compounds with meso-tartrate groups												
Tartaric acids												
meso-$C_4H_6O_6 \cdot H_2O$ (triclinic)	1.536(12)	1.517(12)	1.203(12)	1.321(12)	1.409(12)	124.5(8)	111.3(8)	123.9(8)	106.9(8)	110.3(8)	111.5(8)	94
		1.517(12)	1.206(12)	1.323(12)	1.418(12)	124.6(8)	111.4(8)	124.2(8)	107.4(8)	112.6(8)	113.0(8)	
meso-$C_4H_6O_6 \cdot H_2O$ (monoclinic)[k]	1.534(12)	1.511(12)	1.213(12)	1.302(12)	1.414(12)	124.7(8)	111.4(8)	120.9(8)	107.9(8)	108.8(8)	108.3(8)	94
		1.521(12)	1.223(12)	1.304(12)	1.415(12)	124.8(8)	114.2(8)	123.8(8)	111.0(8)	112.6(8)	112.9(8)	
meso-$C_4H_6O_6$ (triclinic)	1.523(20)	1.520(20)	1.212(20)	1.307(20)	1.413(20)	122.5(14)	113.0(14)	121.8(14)	106.9(14)	108.6(14)	110.6(14)	94
		1.520(20)	1.222(20)	1.341(20)	1.414(20)	125.3(14)	113.0(14)	124.3(14)	108.2(14)	109.6(14)	115.0(14)	
Average for meso acids[c]:	1.531(5)	1.518(3)	1.213(6)	1.316(12)	1.414(2)	124.4(6)	112.4(10)	123.2(12)	108.0(8)	110.4(14)	111.9(18)	
Divalent tartrate salts[d]												
K$_2$ *meso*-$C_4H_4O_6 \cdot 2H_2O$	1.51(2)	1.50(2)	1.27(2)	1.28(2)	1.40(2)	120(2)	117(2)	119(2)	112(2)	109(2)	111(2)	95
		1.51(2)	1.30(2)	1.30(2)	1.42(2)	124(2)	117(2)	123(2)	114(2)	112(2)	114(2)	
Rb$_2$ *meso*-$C_4H_4O_6 \cdot 2H_2O$[f]	1.49	1.51	1.24	1.25	1.38	123	115	118	112	110	111	95
		1.52	1.25	1.28	1.40	127	119	118	113	111	114	
Average for divalent tartrate salts[c]:	1.50(1)	1.51(1)	1.26(2)	1.28(1)	1.40(1)	124(2)	117(1)	120(2)	113(1)	110(1)	112(2)	

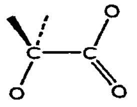
---

[a] Bond lengths are in Ångstroms and angles, in degrees. Where known, the e.s.d. of the last figure is in parentheses. [b] The assignments of the protonated oxygen atoms are those given in *Structure Reports for 1951*[96]. [c] Unweighted average with mean absolute deviation. [d] Bond lengths 3 and 4 and bond angles II and III are differentiated for these compounds according to whether the parameter involves a carboxyl oxygen on the same side of the tartrate chain as the α-hydroxy oxygen or on the opposite side and not according to which carboxyl oxygen, if any, is protonated (see Figure at top of Table). The latter criterion was used to differentiate these bonding parameters for the free acids; however, with only one exception (see footnote k), the protonated carboxyl oxygens of the tartaric acids lie opposite the α-hydroxy group. [e] These parameters involve the ionized carboxyl group. [f] The bonding parameters were calculated from the reported atomic positions. [g] The *z* coordinate of O(4) reported in the original paper as 0.496 fractional cell units[89] is obviously in error. The *z* coordinate of 0.388 used in the calculations was taken from data for the isomorphous ammonium salt[88]. [h] The crystal structure determination gives no indication of which oxygen is protonated. [i] The accuracy of this analysis is low. [j] The parameters for Na K *d*-$C_4H_4O_6 \cdot 4H_2O$[92] were omitted owing to the relatively low accuracy of this analysis. [k] One of the protonated oxygen atoms in this structure lies adjacent to the α-hydroxy oxygen. This is the only tartrate structure which is known to exhibit such a configuration.

whether metal ions or protons are attached to the tartrate group oxygen atoms, the corresponding carbon atom–oxygen atom distances are essentially the same. The carbon atom–uncoordinated carboxyl oxygen atom distances in the dimeric complexes (average, 1.25 Å) indicate a double-bonded (carbonyl) group. It is interesting to note that the geometry of the tartrato(4-) ligands might be considered anomalous in one respect. In these ligands, the carbonyl group of the carboxyl residue is on the side of the tartrate chain *opposite* to that of the α-hydroxyl oxygen atom. In contrast, in all tartrate compounds containing unionized carboxyl groups, with only one known exception[94], the carbonyl (unprotonated) oxygen atom of that group is *adjacent* to the α-hydroxyl oxygen atom:



Tartrato (4-) ligands



Free tartrate groups

E. STABILITIES AND COORDINATION GEOMETRIES OF THE TARTRATO(4-)-BRIDGED-DIMERS —AN HYPOTHESIS

(i) *Observations*

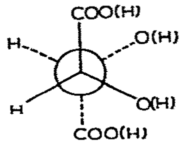
In preceding sections of this article, some observations on the relative stabilities and coordination geometries of the tartrato(4-)-bridged dimers have been presented. These observed features were:

1. *Meso*-tartrate apparently does not form stable binuclear tartrato(4-)-bridged complexes with either vanadyl(IV) or antimony(III).
2. The vanadyl(IV) tartrato(4-)-bridged dimer containing two different tartrate enantiomers (the *dl*, racemic, *cis* isomer) is more stable than the vanadyl(IV) dimer containing two ligands of the same enantiomeric form (the *dd* or *ll*, active, *trans* isomer).
3. In the antimony(III) tartrate system, there is evidence that, in contrast to the corresponding vanadyl(IV) system, a *dl* dimer is less stable than the *dd* (or *ll*) isomer.
4. All of the *dd*-type binuclear structures which have been determined, whether of antimony(III) or vanadyl(IV), exhibit a pseudo-trigonal-bipyramidal coordination geometry. The *dl* vanadyl(IV) complex, however, is square pyramidal.

In this section, we shall propose an explanation for these relative stabilities and geometries. It is necessary first to discuss further some features of tartrate group conformations.

(ii) *Conformations of tartrate groups*

Rotation about carbon(sp^3)-carbon(sp^3) bonds permits a variety of conformations for the tartrate group. For active (*d* or *l*) tartrate groups, however, and similarly for *meso*-tartrate groups, only one conformation has been found in the solid state by X-ray diffraction techniques. The conformational isomer found for the active tartrates has the carboxyl groups opposite each other and is staggered (Fig. 10). The dihedral angles (the staggering angles between the various atoms attached to the tetrahedral carbon atoms as observed when sighting along the central carbon–carbon bond) are, therefore, ideally 60 and 180 deg.



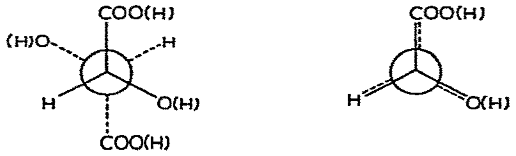


Fig. 10. Conformation of *d*-tartrate groups found in the solid state by X-ray methods. (Left).
Fig. 11. The two possible symmetric conformers of *meso*-tartrate. (Right).

It is perhaps surprising that the conformation found for *meso*-tartrate groups is neither of the two possible symmetric structures (Fig. 11) often invoked to explain the optical inactivity of *meso*-tartrate compounds. In all X-ray structure determinations of *meso*-tartrates carried out thus far[94,95], racemic mixtures of two asymmetric rotamers have been found (Fig. 12). The conformation is again staggered, as expected, but the carboxyl groups are adjacent rather than opposite each other as in the active tartrate isomer. Presumably this enantiomeric pair is also the principal species in *meso*-tartrate solutions. Although it is doubtful that they could be resolved, owing to the expected rapid interconversion, the use of an optically active base has been proposed for separating these enantiomers in the solid state[95].

Table 7 gives the dihedral angles calculated from X-ray structural data for both coordinated and uncoordinated tartrate groups. Dihedral angles involving the hydrogen atoms bonded to the sp^3 carbon atoms are not given as the positions of these hydrogens were not determined, at least with any degree of accuracy, for most of the tartrate structures reported. Owing to small deviations from a tetra-

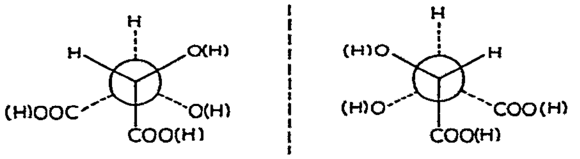
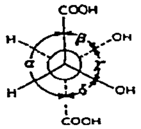


Fig. 12. Enantiomers of *meso*-tartrate groups found in the solid state by X-ray methods.

hedral geometry about the nominally sp^3 carbon atoms (presumably due to imperfect hybridization, intramolecular steric effects, and crystal packing forces), one must examine the dihedral angles *in toto* for a particular compound in order to evaluate the conformation exhibited by the tartrate group present. No single specific angle listed in Table 7 suffices as a determining parameter in comparisons of,

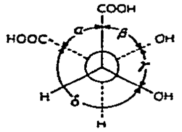
TABLE 7

DIHEDRAL ANGLES OF TARTRATE GROUPS

Compound	*Dihedral angles*[a]				*Ref.*
	α	β	γ	δ	
Compounds with active tartrate groups					
					
Tartrato(4-)-bridged dimers					
Vanadyl(IV)					
$(NH_4)_4[(VO)_2(d\text{-tart})_2] \cdot 2H_2O$					22
tart 1[b]	198	37	88	37	
tart 2	201	48	64	48	
$Na_4[(VO)_2(d\text{-tart})(l\text{-tart})] \cdot 12H_2O$	183	59	62	57	23
Antimony(III)					
$dl\text{-}(NH_4)_2[Sb_2(tart)_2] \cdot 4H_2O$	192	36	86	46	44
$l\text{-}Fe(phen)_3[Sb_2(d\text{-tart})_2] \cdot 8H_2O$					45
tart 1[b]	191	48	73	48	
tart 2	189	51	68	51	
$K_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$					46
tart 1[b]	179	53	79	49	
tart 2	186	45	86	43	
$(NH_4)_2[Sb_2(d\text{-tart})_2] \cdot 3H_2O$[c]					47
tart 1[b]	190	351	102	78	
tart 2	202	20	85	53	
$dl\text{-}K_2[Sb_2(tart)_2] \cdot 3H_2O$[d]					48
tart 1[b]	190	41	84	45	
tart 2	194	45	82	39	
Average for Sb compounds[e,f]:	189(3)	46(4)	80(5)	46(3)	
Tartaric acids and salts					
Tartaric acids					
$d\text{-}C_4H_6O_6$	175	60	58	66	86
$dl\text{-}C_4H_6O_6 \cdot H_2O$	180	61	64	54	87
Average for acids[e]:	178(3)	60(1)	61(3)	60(6)	
Bitartrate salts[g]					
$NH_4\ H\ d\text{-}C_4H_4O_6$	181	53	69	57	88
$Rb\ H\ d\text{-}C_4H_4O_6$[h]	182	55	69	55	89
$NH_4\ H\ dl\text{-}C_4H_4O_6$	182	51	68	58	90
Average for bitartrates[e]:	182(1)	53(2)	69(1)	57(2)	

[continued]

TABLE 7 *(continued)*

Compound	*Dihedral angles*[a]				*Ref.*
	α	β	γ	δ	
Divalent tartrate salts					
Li NH_4 *d*-$C_4H_4O_6 \cdot H_2O$	169	68	54	70	91
Na K *d*-$C_4H_4O_6 \cdot 4H_2O$[i]	179	50	74	57	92
Na K *dl*-$C_4H_4O_6 \cdot 4H_2O$	180	57	86	38	93
Li NH_4 *dl*-$C_4H_4O_6 \cdot H_2O$[j]	181	65	60	54	90
Na_2 *d*-$C_4H_4O_6 \cdot 2H_2O$	183	53	69	55	140
Sr *d*-$C_4H_4O_6 \cdot 3H_2O$[j]	170	73	49	68	141
Ca *d*-$C_4H_4O_6 \cdot 4H_2O$	178	57	68	57	141
Average for divalent tartrate salts[e]:	177(4)	60(7)	66(10)	57(7)	
Compounds with meso-tartrate groups					
Tartaric acids					
meso-$C_4H_6O_6 \cdot H_2O$ (triclinic)	73	48	71	167	94
meso-$C_4H_6O_6 \cdot H_2O$ (monoclinic)[k]	75	47	73	164	94
meso-$C_4H_6O_6$ (triclinic)	75	46	71	167	94
Average for tartaric acids[e]:	74(2)	47(1)	72(1)	166(2)	
Divalent tartrate salts					
K_2 *meso*-$C_4H_4O_6 \cdot 2H_2O$[l]	63	66	61	170	95
Rb_2 *meso*-$C_4H_4O_6 \cdot 2H_2O$	66	62	63	169	95
Average for divalent tartrate salts[e]:	64(2)	64(2)	62(1)	170(1)	

[a] In degrees. Calculated from the reported atomic positions. [b] There are two crystallographically nonequivalent tartrate groups present. [c] The atomic coordinates reported for this compound[47] appear to be highly inaccurate. [d] Partially refined structure. [e] Unweighted average with mean absolute deviation in parentheses. [f] The dihedral angles calculated for the active ammonium antimony tartrate salt[47] were not included in the average (see footnote c). [g] The angle β given for the active ammonium and rubidium bitartrates involves the carbon atom of the unionized carboxyl group. In the racemic ammonium compound, there is no indication of which carboxyl group is ionized. [h] The z coordinate of 0(4), reported in the original paper as 0.496 fractional cell units[89], is obviously in error. A z coordinate of 0.388 was taken from data for the isomorphous ammonium hydrogen salt[88] and was used in calculating the angles β and γ. [i] The accuracy of this analysis is low. [j] Errors are apparent in the coordinates reported for some atoms in these structures. Accordingly, corrected or redetermined atomic positions, obtained from the authors of the original papers, were used in these calculations (see footnotes s and t, Table 4). [k] The monoclinic-monohydrate form of *meso*-tartaric acid is the only tartrate compound known to have a protonated carboxyl oxygen atom adjacent to the α-hydroxyl oxygen atom. The angle β involves this unique group. [l] The x coordinates of 0(1) and 0(4), which are reported as 0.8852 and 0.8534 fractional cell units[95], are in error[97]. Corrected values of 0.8552 and 0.8354 were used in these calculations.

e.g., the degree of staggering for different tartrate groups. The dihedral angle between the carboxyl groups (α in Table 7) appears to vary to a much smaller degree within a particular class of tartrate compounds than do the other angles. This angle is apparently less sensitive to an imperfect tetrahedral geometry about the central carbon atoms and the information imparted by comparisons of this angle should perhaps be weighted accordingly.

(iii) *An hypothesis*

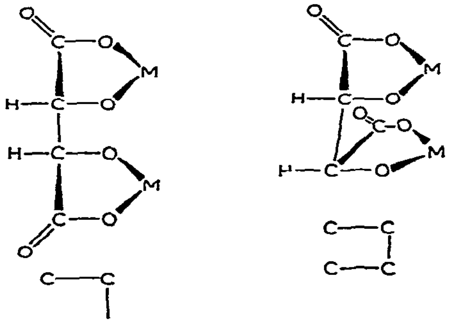
We have already noted that molecular models of dimers containing two *meso*-tartrate groups can be constructed with either a *cis* or a *trans* coordination geometry (Fig. 6). In both cases, however, independent of whether the coordination geometry is pseudo-trigonal-bipyramidal or square-pyramidal (as observed, respectively, in the *dd* and *dl* dimers), the conformation exhibited by the tartrate groups would be the eclipsed conformation shown on the right in Fig. 11.

Similarly, examination of models constructed using active tartrate groups indicates that in dimers containing one *d* and one *l* bridging group (the *cis* isomer), a nearly perfectly staggered conformation is attained if the geometry is square-pyramidal but that as the coordination geometry is distorted toward a trigonal bipyramid, the dihedral angle between adjacent atoms in the tartrate groups decreases steadily (to about 5 deg. for a perfect trigonal bipyramid). Just the reverse behavior is indicated for dimers containing two tartrate groups of the same enantiomeric form (the *trans* isomer). In a *dd*- (or *ll*-) type binuclear tartrato(4-)-bridged complex, a small dihedral angle (about 13 deg.) between adjacent atoms is predicted for a square-pyramidal coordination geometry but the angle increases as the geometry is distorted toward a trigonal bipyramid. The molecular models indicate, however, that in an active dimer, perfect staggering is not realized by the tartrate groups even for an ideal trigonal-bipyramidal geometry.

The data presented in Table 7 substantiate some of these predictions. The tartrato(4-) bridging ligands in the racemic vanadyl(IV) complex are very nearly perfectly staggered. The tartrate groups in the *dd* isomers of vanadyl(IV) and antimony(III), on the other hand, exhibit a significant deviation from a staggered conformation, though in no instance (except, perhaps, in the ammonium antimony(III) *d*-tartrate salt, whose structure[47] is very imprecisely determined) can the bridging groups be described as eclipsed. Moreover, the conformations of the ligands in the active dimers are much less staggered than are those observed for uncoordinated tartrate groups.

A binuclear structure requires either active or *meso*-tartrate groups to possess configurations similar to, though not identical with, those found for uncoordinated tartrate groups. Thus in order for two active tartrate groups to bridge a pair of metal ions, the carboxyl groups must be opposite each other (Fig. 10). Similarly, a *meso*-tartrate-containing dimer constrains the bridging groups to exhibit a conformation which is close to that found for uncoordinated *meso*-tartrate groups—*i.e.*, where the two carboxyl groups are adjacent (Fig. 12). For the *meso* complex, however, the carboxyl groups must not only be adjacent but they must be eclipsed. One can visualize these two situations as shown in Fig. 13. Here we see that in an hypothetical *meso*-tartrate-containing binuclear species, the carbon chain must be folded back upon itself in order for the ligand to achieve coordination.

If a staggered conformation of the tartrate group is a significantly lower energy form, as would be consistent with the structural data presented in Table 7, a cause of the apparent instability of vanadyl(IV) and antimony(III) *meso*-tartrate-containing dimers can now be postulated. These dimers do not form because they would have an unfavorable eclipsed conformation for the bridging ligand.



Active tartrate

meso-tartrate

Fig. 13. Conformations required for the bridging of two metal ions by active and *meso*-tartrate groups. The totally eclipsed *meso* form is distorted for clarity in the drawing.

A similar argument may be advanced to explain the severe distortion observed for the coordination geometry of the active vanadyl(IV) tartrate dimer relative to the geometries observed for other vanadyl(IV) complexes, in particular, the α-hydroxy-carboxylates (Table 1). Since a square-pyramidal geometry would give a nearly eclipsed tartrate group conformation in a *dd* tartrato(4-)-bridged dimer, we propose that a square-pyramidal geometry is unfavorable for this isomer and that the vanadyl(IV) *d*-tartrate complex therefore distorts toward a trigonal bipyramid in order to achieve a more favorably staggered tartrate bridge. Since such a distortion would be expected to result in a loss of coordination energy, the *dd* vanadyl(IV) tartrate complex ought to be less stable than the *dl* complex as is observed. We should note that the difference in stability for the vanadyl(IV) *dd* and *dl* dimers cannot be explained by *cis-trans* effects. Spectral studies indicate that monomeric vanadyl(IV) α-hydroxycarboxylates always occur as the *trans* isomer[23,26,28,29], which thus would seem to be generally more stable than the *cis*. Just the reverse ordering, however, is found for the vanadyl(IV) tartrates.

For four-coordinate complexes of trivalent antimony, a trigonal-bipyramidal geometry is apparently preferred (Table 2). As we have seen, such a geometry would give an unfavorable conformation to the ligands in a *dl* dimer, which therefore ought to be unstable towards disproportionation to the *dd* and *ll* isomers. Thus the apparent stability ordering for the antimony(III) tartarte system is *dd* or *ll* > *dl*.

In summary, the following proposals are advanced:

1. Tartrato(4-)-bridged dimers of vanadyl(IV) and antimony(III) containing *meso*-tartrate groups are unstable because their formation requires an unfavorable eclipsed conformation for the bridging ligands.
2. The *dd* vanadyl(IV) tartrate dimer is distorted at the cost of some coordination energy towards a trigonal-bipyramidal coordination geometry in order to achieve a more staggered conformation for the tartrate groups. Even with such a distortion, however, perfect staggering is not realized by the bridging groups.
3. In the antimony(III) tartrate system, the *dl* dimer is unstable towards disproportionation to the *dd* and *ll* dimers because the trigonal-bipyramidal coordination geometry favored by four-coordinate trivalent antimony gives a more eclipsed conformation to the ligands in a racemic isomer than to those in the active isomer.

We wish to point out that somewhat similar arguments (*i.e.*, based on "preferred conformation" [144]) have been advanced to explain stereospecific effects in other metallochelate systems [145].

There is another possible explanation for the absence of *meso*-tartrate-containing dimers. It may be that the ionizable protons in *meso*-tartaric acid are less acidic than those in the active isomer. If this were true, the absence of a *meso*-tartrate binuclear complex could just be due to the higher pH required for formation of the tartrato(4-) ligand. In a higher pH region, there is more opportunity for hydroxide ions to compete successfully with the *meso*-tartrate for coordination with antimony(III) or vanadyl(IV). It is known that the acid dissocation constants for ionization of the carboxyl groups in *meso*-tartaric acid are smaller than the corresponding constants for *d*-tartaric acid (at 25 °C, $K_1 = 0.60 \times 10^{-3}$, $K_2 = 1.53 \times 10^{-5}$ for *meso*-tartaric acid; $K_1 = 1.04 \times 10^{-3}$, $K_2 = 4.55 \times 10^{-5}$ for *d*-tartaric acid[100]); however, no dissociation constants for proton removal from the α-hydroxyl groups of the *meso* isomer have been reported, although these constants are known for the active isomer (approximately 10^{-14} and 3×10^{-16} for K_3 and K_4[101]). Even if all of the acid dissociation constants were known for *meso*-tartaric acid, it might be difficult to evaluate the effect of different acidities on the relative complexing abilities of the two tartrate isomers.

F. EVIDENCE FOR ADDITIONAL TARTRATO(4-)-BRIDGED BINUCLEAR STRUCTURES

Tartrates complex with many metal ions other than vanadyl(IV) and antimony(III) to give "emetic-type" salts (compounds whose stoichiometries or properties indicate that one or both tartrate hydroxyl protons may be ionized)[102]. A common feature of these compounds is that the metal-ligand ratio[1,103] is usually 1:1. The following is a brief discussion of evidence for additional tartrato(4-)-bridged dimeric complexes in some of these other metallotartrate systems.

(i) *Chromium(III) tartrates*

A tartrato(4-)-bridged binuclear structure has recently been postulated for two mixed chromium(III) complexes[104]. These species are proposed to contain two chromium(III) ions bridged by two quadridentate *d*-tartrate ligands with the other two coordination positions on the metal ions filled by bidentate ligands (2,2′-dipyridyl or 1,10-phenanthroline). Owing to the restrictions imposed by the binuclear structure, only a Λ-Λ absolute configuration[105] about the chromium(III) ion is possible when the bridging ligands are of the *d*-enantiomeric form. It would be interesting to determine whether a *dl* dimer can form, since the tartrate coordination geometry in this distorted octahedral system is quite similar to that in pseudo-trigonal-bipyramidal compounds, the equatorial angle here being nearer to 90° than 120°. Following the reasoning outlined previously, we would expect the *dl* dimer to have an unfavorable conformation of bridging ligands.

(ii) *Arsenic(III) and bismuth(III) tartrates*

Both arsenic(III)[106] and bismuth(III)[107–109] form "tartar-emetic-type" salts, to which have been assigned the formulae $\mathrm{M[AsOC_4H_4O_6]\cdot xH_2O}$ and $\mathrm{M[BiOC_4H_4O_6]\cdot xH_2O}$, where M is a univalent cation. These formulae are similar to those advanced at one time for the antimony(III) tartrate salts[35,36]. It has been noted that the bismuth salts can be dehydrated to give crystalline materials[107,108] with the general formula $\mathrm{M[BiC_4H_2O_6]}$. Moreover, potassium bismuth(III) tartrate, $\mathrm{KBiC_4H_5O_{7.5}}$, has an empirical formula which is the same (except for the metal ion) as that of normal tartar emetic[110] and a stable crystalline ammonium salt with a formula $\mathrm{NH_4[BiC_4H_2O_6]}$ has been isolated from an aqueous medium[111]. One is tempted to speculate that all of the members of the trivalent arsenic family (As, Sb, Bi) form tartrato(4-) binuclear complexes, particularly as both trivalent bismuth[63,112] and arsenic[113] exhibit pseudo-trigonal-bipyramidal fourfold coordinations to oxygen atoms and these coordinations possess a geometry very similar to that found in the antimony(III) tartrates. Furthermore, both arsenic(III)[114] and bismuth(III)[115] are reported to give no tartar-emetic-type compounds with *meso*-tartrate under the same conditions used for synthesis of the corresponding *d*-tartrate compounds. Finally, there is an unconfirmed report, based on an old study of the relative crystal morphologies, that one of the arsenic tartrate salts is isomorphous with potassium antimony(III) *d*-tartrate[106], which is now known to contain dimeric anions[46].

The arsenic(III) and bismuth(III) tartrates have been only poorly characterized. Investigations of these compounds are presently in progress in this laboratory.

(iii) *Antimony(III) α,α′-dimercaptosuccinate salts*

α,α′-dimercaptosuccinic acid (HOOCCHSHCHSHCOOH), a mercapto analog of tartaric acid, complexes readily with many metal ions[116]. Among the complexes formed is a pharmaceutically important[117] antimony(III) complex isolated as the sodium salt, $Na[Sb(OH)C_4H_3O_4S_2]$[118]. Since this salt has not been well-characterized, an empirical formula of $Na[SbC_4H_2O_4S_2] \cdot H_2O$ could just as well be advanced for this compound. A totally ionized ligand is indicated since mercapto groups are much more acidic than hydroxy groups[139]. Furthermore, thioglycollic acid ($CH_2SHCOOH$) is known to ionize completely upon coordination with antimony(III) to give the salt, hydrogen bis(thioglycollato(2-))antimonate(III). This thioglycollate derivative exhibits a *trans* pseudo-trigonal-bipyramidal coordination geometry with the carboxyl oxygen atoms in axial sites and the α-mercapto groups in the equatorial positions[72]. This geometry is precisely that required to form a hypothetical α,α′-dimercaptosuccinato(4-)-bridged binuclear complex. It has been reported that the *meso*-dimercapto ligand is a much stronger complexing ligand toward antimony(III) than is *d*-tartaric acid and it has been proposed that the product is dimeric[119]. Arsenic(III) is also reported to give salts with this mercapto derivative of tartaric acid[120].

(iv) *Copper(II) tartrates*

The structures of the copper(II) complexes present in Fehling's solution are not at all certain[2]. Among the many crystalline compounds reportedly isolated from basic copper(II) tartrate solutions are salts having the formula[121] $M_2[CuC_4H_2O_6] \cdot xH_2O$. No extensive studies of these compounds have yet been reported. The presence of polynuclear complexes in this system has been implied by potentiometric titrations[122] and by spectral differences between active and racemic copper tartrate solutions at higher pH[21]. It is interesting that similar spectral differences were the first indication of the existence of tartrato(4-)-bridged dimers in the vanadyl(IV) tartrate system[20]. Colligative properties of basic copper(II) tartrate solutions indicate a dimeric species[51]. Racemic copper(II) tartrate salts with the formula $M_2[CuC_4H_2O_6] \cdot xH_2O$ are reported to be more stable than the corresponding active compounds[123]. It should be noted that just such a stability difference would be predicted if these compounds contained tartrato(4-)-bridged dimeric complexes since the square-planar coordination geometry normally exhibited by copper(II) should give a better staggering angle to the bridging groups in a *dl* dimer than in a *dd* dimer. There is a single report[124], however, that *meso*-tartrate complexes as readily as the *d*-enantiomer with copper(II) and gives solid salts similar to these described above.

(v) *Other potential tartrato(4-)-bridged binuclear complexes*

Thorium(IV) combines with tartaric acid to give species in which the α-hydroxyl groups are apparently ionized[125] and a tartrato(4-)-bridged dimeric structure has been proposed[126]. Praeseodymium is reported to give complexes containing tetranegative, quadridentate tartrate ligands[127], and binuclear species have been proposed[128]. Iron(III) tartrate solutions have been postulated to contain dimers in which the tartrate ligand is quadridentate[129]. Polynuclear structures containing both chromium(III) and indium(III) or tin(II) have also been suggested[130]. It is interesting to note that a similar mixed-metal binuclear structure containing both copper(II) and chromium(III) ions has been advanced for a citrate complex[131]. A diamagnetic binuclear rhenium(IV) tartrate complex has reportedly been isolated as the potassium salt[132].

Potentiometric titrations indicate that tungsten(VI) forms a 2:2 complex with tartaric acid at higher pH in aqueous solution[133] and a crystalline material, $Na_4[WO_3C_4H_2O_6] \cdot 8H_2O$, which is dehydrated completely at 105°, can be isolated[134]. The X-ray powder patterns of both the hydrated and anhydrous tetrasodium tungsten(VI) tartrates differ completely from those of sodium tungstate dihydrate and sodium tartrate dihydrate[134]. Although α-hydroxy acids complex readily with tungsten(VI), β-hydroxy acids apparently do not[135]. This observation indicates that the hydroxyl oxygens are involved in the bonding of the tungsten(VI) tartrate complex.

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