^{13}C NMR Studies on Arsenic(III) and Antimony(III) Dihydroxydicarboxylate Complexes

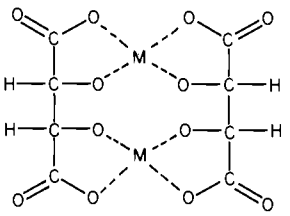
Dragoslav Marcovich and Robert E. Tapscott*

Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131. *Received March 28, 1980*

Abstract: Sodium salts of the anionic complexes of tartrate(4-) and its methyl-substituted derivatives with arsenic(III) and antimony(III) have been prepared and the stereochemistries in aqueous solution studied by ^{13}C NMR spectroscopy. The compounds containing (±)-tartrate(4-), *threo*-monomethyltartrate(4-), and (±)-dimethyltartrate(4-) are binuclear in solution with *dd* and *ll* forms more stable than the *dl*. Both proximal-methyl and distal-methyl isomers are observed for the *threo*-monomethyltartrate(4-)-bridged dimers. ^{13}C-^{1}H coupling through at least five bonds is observed in spectra of the tartrate(4-) complexes. Spectra of the mixed As/Sb complexes, which are formed in metal exchange reactions with remarkably slow kinetics in at least one system, indicate that geometrical distortions, unaccompanied by major changes in nonbonded interactions, significantly influence the ^{13}C NMR chemical shifts. Solid salts of arsenic(III) with *ms*-dimethyltartrate(4-) and with *erythro*-monomethyltartrate(4-) have also been prepared. While there is strong evidence for the presence of a C_2-symmetry *ms-ms* dimer in solutions of the former compound, solutions of both salts contain a mixture of species. Complexes of antimony(III) with meso or erythro ligands are apparently much less stable than those of arsenic(III).

Introduction

The structure of the anionic complex present in potassium antimony(III) tartrate ("tartar emetic") and related salts was long debated before a series of crystal-structure determinations[1-7] demonstrated conclusively the presence of the binuclear tartrate(4-)-bridged complex **1**. A similar structure has also been



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found for an arsenic(III) tartrate salt.[8] Despite the availability of crystal-structure data, however, the salts of these binuclear complexes are still often incorrectly named or formulated as monomeric compounds, usually assumed to contain the SbO^+ or AsO^+ ion.[9-11]

Binuclear tartrate-bridged complexes can exist in several diastereomeric forms, depending upon the isomeric composition of the bridging ligands—which can be *d* [(*R*,*R*) or (+)], *l* [(*S*,*S*) or (-)], or meso (*R*,*S*).[12] Steric considerations permit the prediction that such complexes of arsenic(III) and antimony(III), with their pseudo-trigonal-bipyramidal coordination geometry,[1] should exhibit the isomer stability ordering *dd* = *ll* > *dl* > *ms-ms*.[13,14] This predicted stability ordering is supported by solid-state structures of antimony(III) complexes with racemic tartrate which have invariably shown the presence of racemic mixtures of *dd* and *ll* structures only (i.e., no *dl* complex) and the absence of successful preparations of antimony(III) *ms*-tartrate complexes.[1,14] Binuclear *ms-ms* isomers have been reported for some chromium(III) tartrate complexes where the octahedral coordination geometry permits the formation of strain-free structures.[15]

The present study was undertaken to characterize the aqueous solution structures of antimony(III) and arsenic(III) tartrates, to further detail the relative isomer stabilities, and to elucidate the stereochemistry of the methyl-substituted derivatives. The characterization of the aqueous solution species of antimony(III) and arsenic(III) tartrates is of particular significance owing to the extensive use of these materials as resolving agents, either through diastereomeric salt formation[10,16,17] or as chromatographic eluents.[18,19] In addition, antimony(III) tartrate salts are valuable anthelmintic agents for the control of schistosomal blood flukes.[20,21] Very few ^{13}C NMR investigations have been reported for diamagnetic α-hydroxycarboxylate complexes.[22-24]

Experimental Section

Ligands. Commercially available (+)-, *ms*-, and (±)-tartaric acid ($C_4H_6O_6$) were used as obtained. Dimethyltartaric acid ($C_6H_{10}O_6$) and monomethyltartaric acid ($C_5H_8O_6$) were prepared and those isomers employed in this study (excepting the enantiomers of $C_6H_{10}O_6$) were

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Table I. Analysis of Arsenic(III) and Antimony(III) Dihydroxydicarboxylates

compd	calcd, %			found, %		
	C	H	H_2O	C	H	H_2O
$Na_2[As_2((+)\text{-}C_4H_2O_6)_2]\cdot 4.5H_2O$[a]	16.90	2.30	14.2	17.00	2.21	14.9[b]
$Na_2[As_2((\pm)\text{-}C_4H_2O_6)_2]\cdot 4H_2O$	17.16	2.16	12.9	16.79[b]	2.20[b]	12.9[b]
$Na_2[As_2((\pm)\text{-}threo\text{-}C_5H_4O_6)_2]\cdot 3H_2O$	21.07	2.48		21.15[b]	2.35[b]	
$Na_2[As_2((\pm)\text{-}erythro\text{-}C_5H_4O_6)_2]\cdot 4H_2O$[c]	20.42	2.74		20.57	2.59	
$Na_2[As_2((+)\text{-}C_6H_6O_6)_2]\cdot 1.5H_2O\cdot 0.5C_2H_5OH$[d]	26.28	3.05		26.36[b]	3.06[b]	
$Na_2[As_2((\pm)\text{-}C_6H_6O_6)_2]\cdot 1.5H_2O\cdot 0.5C_2H_5OH$[d]	26.28	3.05	4.6	26.59[b]	3.23[b]	5.2[b]
$Na_2[As_2(ms\text{-}C_6H_6O_6)_2]\cdot 5H_2O$	22.73	3.50		22.48	3.51	
$Na_2[Sb_2((+)\text{-}C_4H_2O_6)_2]\cdot 4H_2O$	14.70	1.85	11.0	14.56	1.97	10.6[b]
$Na_2[Sb_2((\pm)\text{-}C_4H_2O_6)_2]\cdot 5H_2O$	14.31	2.10	13.4	14.13[b]	2.10[b]	13.0[b]
$Na_2[Sb_2((\pm)\text{-}threo\text{-}C_5H_4O_6)_2]\cdot 2.5H_2O$	18.34	2.00	6.9	18.15[b]	1.75[b]	7.1[b]
$Na_2[Sb_2((+)\text{-}C_6H_6O_6)_2]\cdot H_2O\cdot 2C_2H_5OH$[d]	25.70	3.50		25.05	3.63	
$Na_2[Sb_2((\pm)\text{-}C_6H_6O_6)_2]\cdot 4H_2O$	20.31	2.84	10.1	20.42[b]	2.42[b]	9.7[b]

[a] Effloresces rapidly. [b] Average of two or more determinations. [c] Obtainable only as a glass. [d] Ethanol detected by ^{13}C NMR spectroscopy.

separated by literature methods.[25-27]

To resolve the dimethyl derivative, quinine 2-hydrate (64.1 g, 178 mmol) and (±)-dimethyltartaric acid (15.9 g, 89 mmol) were separately dissolved in 800 mL of methanol each and the warmed solutions were mixed. Upon cooling, 25.1 g of white, crystalline material separated. Sufficient sodium hydroxide solution was added to a solution of the collected solid in water to give a basic mixture. The quinine was filtered off and the filtrate was extracted several times with chloroform to remove dissolved quinine. The solution was acidified with concentrated hydrochloric acid and evaporated to dryness on a rotary evaporator, and the dry residue was extracted with acetone. The first crop of crystal obtained, upon evaporation of the acetone, was racemic material while the last crop obtained (6.4 g) was essentially pure (−)-dimethyltartaric acid. Workup of the filtrate, after removal of the quinine salt of (−)-dimethyltartrate, in a similar manner gave (+)-dimethyltartaric acid. The isomers were recrystallized from ethyl acetate (solubility in 100 g of ethyl acetate at 25 °C: (±)-$C_6H_{10}O_6$, 1.34 g; (+)-$C_6H_{10}O_6$, 7.02 g). The molar rotations were in good agreement with those previously reported.[27] The optical purities were easily checked since there are large IR spectral differences between racemic and resolved dimethyltartaric acid. IR (KBr) characteristic peaks: (±)-$C_6H_{10}O_6$, 640, 3523, 3537 cm^{-1}; (+)- and (−)-$C_6H_{10}O_6$, 953, 1322 cm^{-1}.

Subsequent work with the resolved compounds showed that the (+) isomer gives as a solid only the 2:1 salt with quinine while the (−) isomer gives only the 1:1 salt. Anal. Calcd for $[C_{20}H_{24}N_2O_6]_2\cdot(+)\text{-}C_6H_{10}O_6$: C, 66.81; H, 7.07; N, 6.88. Found: C, 66.90; H, 7.05; N, 6.85. IR(KBr): 833 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2O_6\cdot(-)\text{-}C_6H_{10}O_6$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.19; H, 6.79; N, 5.60. IR (KBr): 780 (s), 170 (m, br) cm^{-1}.

Satisfactory elemental analyses were obtained for all of the methyl-substituted tartaric acid isomers prepared. All melting points were in agreement with literature values.[27]

Disodium salts of the substituted and unsubstituted tartaric acids (with the exception of sodium (+)-tartrate 2-hydrate, which was commercially available) were obtained by addition of 95% ethanol to aqueous solutions of the appropriate acids that had been neutralized with sodium hydroxide. The salts were filtered off, redissolved in water, reprecipitated by addition of ethanol, washed with ethanol and acetone, and air dried. Satisfactory elemental analyses were obtained for all of the salts prepared.

Sodium Arsenic(III) and Antimony(III) Tartrate and Methyl-Substituted Tartrates. All the complex salts were prepared by heating aqueous slurries of arsenic(III) oxide (As_2O_3) or antimony(III) oxide (Sb_2O_3) with NaOH and the dihydroxydicarboxylic acid in a molar ratio of 1:2:2 on a steam bath for 12 h to several days. The oxide residues (usually very slight for the arsenic derivatives) were removed by filtration and the white, crystalline salts were precipitated by careful addition of 95% ethanol to the warmed solutions. Neither oxide reacted with *ms*-tartrate (as evidenced by no significant dissolution) and Sb_2O_3 failed to react with *ms*-dimethyltartrate or with *erythro*-monomethyltartrate. The compounds were filter collected, washed with aqueous ethanol and acetone, and air dried. The analyses are given in Table I.

Physical Measurements. Natural abundance ^{13}C NMR spectra were recorded at ca. 35 °C on a Varian XL-100/Nicolet TT-100 FT system, with an observed frequency of 25.2 MHz. All ^{13}C NMR spectra were obtained by using a 3000-Hz sweep width (300 Hz for expanded spectra of specific regions), 1.5 s acquisition time, 15-μs pulse width, and no pulse delay. Both proton-coupled and proton-decoupled (noise-modulated decoupling) spectra were collected. For the NMR samples, 1.0 mmol of material (0.50 mmol of each complex salt in the case of the mixed-metalloid systems) was dissolved in 5.0 mL of D_2O and placed in a 12-mm sample tube. Tetramethylsilane was used as an external standard in a coaxial 5-mm tube. For a few of the unsubstituted tartrate compounds, a 23% aqueous solution of dioxane was employed as an external reference but the chemical shifts were recalculated relative to Me_4Si (δ 67.60). Duplicate runs using Me_4Si as a reference gave δ values agreeing within 0.05 ppm with those calculated from the dioxane-referenced spectra. An accuracy of ±0.05 ppm is estimated for all reported chemical shifts. Computer simulations of some spectral regions were made by using the ITERCAL program provided by Nicolet Technology Corp. on the NIC-80 data processor.

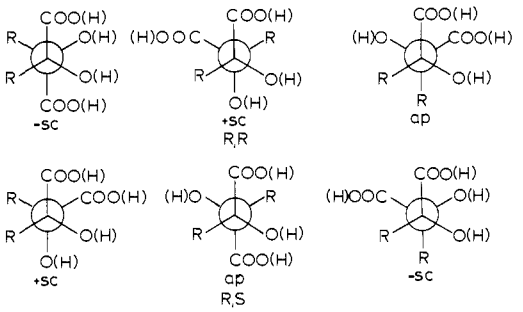

Figure 1. Conformers of tartrates and their derivatives.

Results and Discussion

Ligand Stereochemistry. The ^{13}C NMR results for the sodium salts of the free dihydroxydicarboxylate ligands in aqueous solution are presented in Table II. The resonances are readily assigned from the chemical shifts[28] and the proton–carbon spin multiplets.

The carboxyl carbon atoms of *ms*-tartrate(2−) exhibit a chemical shift (δ) and a vicinal proton–carbon coupling constant ($^3J_{CH}$) which are respectively smaller and larger than those of the active isomer. This is consistent with the predominant aqueous solution conformers (Figure 1) being (−)-synclinal[29] for (+)-tartrate(2−) and (±)-synclinal for *ms*-tartrate(2−) as found in all solid-state structures of the acids and their simple salts to date.[1] The smaller carboxyl carbon δ value of the meso isomer is then attributed to a greater upfield shift owing to a larger number of gauche interactions in this isomer between the carboxyl groups and nonhydrogen atoms (i.e., a gauche γ effect from whatever mechanism[30,31]). The larger vicinal coupling constant of the meso isomer carboxyl carbon is due to the 180° dihedral angle, where $^3J_{CH}$ is expected to be a maximum,[32] between one carboxyl group

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Table II. ^{13}C NMR Parameters for Dihydroxydicarboxylates and Their Arsenic and Antimony Complexes

compd	δ, ppm [J_{CH}, Hz] >CHC*OO	$H_2C(>C)C^*OO$	>C*HO(H)	$H_3C(>C^*)O(H)$	C^*H_3
		Free Ligands			
$Na_2(+)$-$C_4H_4O_6$	179.34 [3.6, 1.6][a]		74.87 [146.2][b]		
Na_2(*ms*)-$C_4H_4O_6$	178.04 [4.8, 4.8][a]		75.88 [146.4, 3.0][a]		
$Na_2(\pm)$-$C_6H_8O_6$		183.49 [3.5][c]		79.23[d]	20.84 [128.2][c]
Na_2(*ms*)-$C_6H_8O_6$		181.74 [3.6][c]		79.46[d]	23.26 [127.9][c]
$Na_2(\pm)$-*threo*-$C_5H_6O_6$	178.70[e]	182.05[e]	77.65 [149.0][b]	78.44 [3.7][c]	23.40 [128.4][c]
$Na_2(\pm)$-*erythro*-$C_5H_6O_6$	178.31 [3.6][b]	181.45 [2.9][b]	77.68 [143.6, 3.7][f]	78.34 [3.4][c]	23.29 [128.7][c]
		Tartrate Complexes			
$Na_2[As_2((+)\text{-}C_4H_2O_6)_2]$	180.04 [3.5, 1.5, 1.5][g]		78.78 [151.6][b]		
$Na_2[As_2((\pm)\text{-}C_4H_2O_6)_2]$	180.03[h]		78.76[h]		
$Na_2[Sb_2((+)\text{-}C_4H_2O_6)_2]$	183.26 [3.1, 1.6, 1.5][g]		78.55 [149.4][b]		
$Na_2[Sb_2((\pm)\text{-}C_4H_2O_6)_2]$	183.25[h]		78.52[h]		
$[SbAs((+)\text{-}C_4H_2O_6)_2]^{2-}$	(Sb)[i] 183.02,[d]		77.19 [149.2],[b]		
	(As)[i] 180.27[d]		80.17 [151.1][b]		
		Dimethyltartrate Complexes			
$Na_2[As_2((+)\text{-}C_6H_6O_6)_2]$		181.85 [3.8][c]		85.07 [3.9][c]	23.70 [129.5][c]
$Na_2[As_2((\pm)\text{-}C_6H_6O_6)_2]$		181.83[h]		85.07[h]	23.72[h]
$Na_2[As_2((ms)\text{-}C_6H_6O_6)_2]$ (?)		181.82 [3.7][c]		86.29[j]	23.47 [130.3][c]
(C_2)		181.36 [3.9],[c]		86.93,[j]	22.73 [128.7],[c]
		181.04 [3.9][c]		85.96[j]	22.62 [128.7][c]
$Na_2[Sb_2((+)\text{-}C_6H_6O_6)_2]$		184.74 [3.6][c]		84.21 [3.6][c]	24.91 [128.7][c]
$Na_2[Sb_2((\pm)\text{-}C_6H_6O_6)_2]$		184.83[h]		84.30[h]	24.96[h]
$[AsSb((\pm)\text{-}C_6H_6O_6)_2]^{2-}$ (Sb)[i]		184.56,[d]		83.02 [3.7],[c]	24.41 [129.5],[c]
(As)[i]		182.09[d]		86.29 [3.7][c]	24.18 [129.0][c]
		Monomethyltartrate Complexes			
$Na_2[As_2((\pm)\text{-}threo\text{-}C_5H_4O_6)_2]$	178.73,[j]	182.84,[j]	80.21 [153],[k]	84.15,[j]	23.54 [130],[c]
	178.85[j]	182.96[j]	80.33 [153][k]	84.24[j]	23.49 [130][c]
$Na_2[Sb_2((\pm)\text{-}threo\text{-}C_5H_4O_6)_2]$	181.92,[j]	185.92,[j]	80.20 [152],[k]	83.25,[j]	25.04[l] [128][c]
	182.00[j]	186.00[j]	80.34 [152][k]	83.40[j]	

[a] Doublet of doublets. [b] Doublet. [c] Quartet. [d] Complex multiplet. [e] Splitting not resolved. [f] Doublet of quartets. [g] J values from spectral synthesis. [h] Proton-coupled spectrum was not run. [i] Ions near which the nonequivalent carbon atoms are located. [j] Overlap prevented accurate determination of proton splittings. [k] Doublet with smaller splitting. [l] Only one peak observed apparently owing to accidental overlap.

Table III. Chemical-Shift Changes upon Coordination

metalloid	Δδ, ppm[a] >CHC*OO	$H_3C(>C)C^*OO$	>C*HO	$H_3C(>C^*)O$	C^*H_3
		(±)-Tartrates			
As	0.7		3.9		
Sb	3.9		3.7		
		(±)-Dimethyltartrates			
As		−1.6		5.8	2.9
Sb		1.3		5.0	4.1
		ms-Dimethyltartrate			
As (?)		0.1		6.8	0.2
(C_2)		−0.4, −0.7		7.5, 6.5	−0.5, −0.6
		threo-Monomethyltartrates			
As	0.0, 0.2	0.8, 0.9	2.6, 2.7	5.7, 5.8	0.1, 0.2
Sb	3.2, 3.3	3.9, 4.0	2.6, 2.7	4.8, 5.0	

[a] $\Delta\delta = \delta$ (complex) − δ (ligand(2−)).

and the vicinal proton in each of the (±)-*sc* conformers.

Smaller values of δ (compared with the racemic and threo isomers) are also observed for the carboxyl carbons of *ms*-dimethyltartrate(2−) and *erythro*-monomethyltartrate(2−). Here, however, the absence of an upfield shift of the methyl resonance upon passing from the monomethyl compound to the dimethyl derivative for the *R,S* isomers (contrast with the large upfield methyl resonance shift observed for the *R,R*; *S,S* system where there is a significant γ effect[33]) indicates that the antiperiplanar conformer population is significant for *ms*-dimethyltartrate(2−) (and perhaps also for *erythro*-monomethyltartrate(2−)). Stabilization of the *ap* conformer of the *R,S* diastereomer by increasing methyl substitution is not unexpected.[34]

Complexes. General Observations. Complexes of arsenic(III) and antimony(III) with dimethyltartrate and monomethyltartrate have not been previously reported. The stoichiometry and resemblance to the corresponding tartrates indicate that the white, crystalline (except for the sodium arsenic(III) *erythro*-monomethyltartrate salt) solids contain 2:2 bridged binuclear complexes with tetranegative ligands—as found in the tartrates.[1-8] ^{13}C NMR chemical shifts indicate that the ethanolate of crystallization present in some salts (Table I) is not coordinated (at least in the solution species). Table II gives solution ^{13}C NMR parameters for all of the complexes studied. The downfield shifts relative to the free ligands observed for all carbinol and most carboxyl resonances (Table III) indicate chelation and proton loss by the

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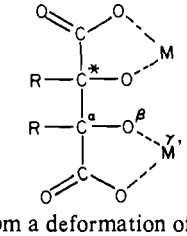
α-hydroxycarboxylate groups.[22,23] Larger shifts are observed for carbon atoms in carboxyl groups coordinated to antimony (compared to those coordinated to arsenic) and for methyl-substituted carbinol carbon atoms. The slightly larger $^1J_{CH}$ values of the arsenic complexes (compared to the antimony derivatives) are consistent with the electronegativity differences between the two metalloid ions.[35]

Table II omits data for very low amplitude resonances (less than 10% of the amplitude of the major peaks) observed upfield from the major peaks in spectra of the arsenic-containing compounds (δ, ppm [$^1J_{CH}$, Hz] = 177.31, 73.95 [146.5] for minor peaks in the solution spectrum of $Na_2[As_2((+)\text{-}C_4H_2O_6)_2]$; 180.5, 79.1, 21.74 [129] with $Na_2[As_2((\pm)\text{-}C_6H_6O_6)_2]$; 179.83, 81.47, 22.07 with $Na_2[As_2(ms\text{-}C_6H_6O_6)_2]$; 176.62, 179.91, 76.51 [147], 77.98, 22.67 [129.1] with $Na_2[As_2((\pm)\text{-}threo\text{-}C_5H_4O_6)_2]$). Considering (1) the $^1J_{CH}$ values, which are close to those obtained for the sodium salts of the free ligands, (2) the chemical shifts, which are significantly upfield from those observed here for arsenic(III) complexes, and (3) the observed superposition of minor and free-ligand peaks upon addition of excess ligand to solutions of arsenic(III) tartrate(4–), we assign the minor peaks to free ligand, whose presence is apparently due to partial dissociation of the arsenic(III) complexes. This assignment is not unequivocal since the chemical shifts of the minor peaks do not match those observed for the pure ligand salts. The experiments with added ligand, however, show that the ^{13}C chemical shifts of excess tartrate(2–) in the presence of arsenic(III) tartrate(4–) and also antimony(III) tartrate(4–) are strongly concentration dependent. On the other hand, the resonance positions of the major peaks are remarkably insensitive to concentration variations and to the presence of added ligand.

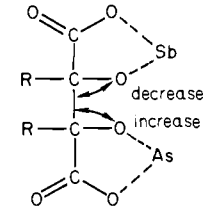
Tartrate(4–) Complexes. The simple two-peaked $^{13}C\{^1H\}$ NMR spectra observed for arsenic(III) and antimony(III) tartrate(4–) salts in aqueous solution are consistent with binuclear structures of D_2 symmetry (as found in the solid state[1-8]) but they do not rule out the possibility of lower symmetry species exhibiting dynamic behavior.[36] The following observations, however, provide proof for the presence of binuclear structures in solution.

The $^{13}C\{^1H\}$ NMR spectrum of an equimolar mixture of arsenic(III) and antimony(III) tartrate(4–) salts contains four new resonances in addition to peaks which are unchanged in position from those of the pure arsenic(III) and pure antimony(III) compounds. We assign the new resonances to a C_2-symmetry mixed As/Sb tartrate(4–)-bridged complex. The assignments given in Table II for the locations (near antimony or near arsenic) of chemically similar carboxyl carbons are based on comparisons of the chemical shifts for the mixed and nonmixed systems. The carbinol assignments are based on $^1J_{CH}$ values which are expected to be influenced most by the metalloid β to the carbon of interest.

Surprisingly large carbinol ^{13}C NMR resonance shifts upfield and downfield accompany the formation of the mixed As/Sb complex from the nonmixed complexes. These shifts, which are very similar to those found for the dimethyltartrate(4–) mixed As/Sb complex (vide infra), result from substitution of one metalloid for another at a site which is γ to the carbinol of interest



and probably arise from a deformation of the binuclear structure owing to the presence of two slightly different coordination geometries. The carboxyl oxygen–arsenic and hydroxyl oxygen–arsenic distances in the arsenic(III) tartrate(4–) structure[8] are about 0.12 and 0.21 Å shorter, respectively, than the corresponding distances in the antimony(III) compound.[1-7] An inspection of molecular models shows that the strain induced by differing coordination bond lengths is best relieved by increasing the angle between the central carbon–carbon bond and the carbon–hydroxyl oxygen bond of the carbinol group near arsenic and decreasing the corresponding angle involving the carbinol near antimony.



Gorenstein[31] has suggested that increases (decreases) in bond angle at an atom owing to γ substitution cause upfield (downfield) ^{13}C γ shifts which most affect that atom and the atom β to it. This mechanism predicts precisely the ^{13}C NMR *pattern* we observe for the heterotopic carbinols of the mixed As/Sb complex (equal (1.4 ppm) and opposite resonance shifts) but not the shift directions (downfield for the carbinol near arsenic where the angle is increased and upfield for the carbinol near antimony where the angle is decreased), at least when applied simplistically. However, Gorenstein has himself pointed out[31] that when one angle at an atom is increased, others must decrease. Moreover, in some cases some correlation has been observed between increasing angle and downfield shifts.[37] Regardless of the exact interpretation, however, it is apparent that bond-geometry distortions are almost certainly involved in the resonance changes observed upon formation of the mixed As/Sb complex (as found for formation of other metallo systems[38]). It is of particular significance that the γ substitutions which result in formation of the mixed complex are expected to be accompanied only by geometrical distortions and not by significant changes in nonbonded steric interactions—an observation which may shed some light on the repulsion/distortion controversy in the explanation of γ effects.[37]

That ^{13}C NMR spectra of the (+)- and (±)-tartrate(4–) binuclear complexes are identical (Table II) demonstrates conclusively the higher stability of the *dd* (and *ll*) isomer compared with a hypothetical *dl* complex in accordance with earlier predictions.[14] No new peaks are observed in spectra of the racemic system, which must consist of an equimolar mixture of *dd* and *ll* isomers, and the spectra remain unchanged for solutions allowed to equilibrate for several months. We estimate that *dl* species at 5% of the abundance of the primary complex could have been detected from the ^{13}C NMR spectra.

Complexation of arsenic(III) by *ms*-tartrate is indicated by our observations that addition of this ligand to a solution of arsenic(III) (+)-tartrate(4–) causes the appearance of several new, sharp resonances (some of which may be due to free *ms*- and/or (+)-tartrate(2–) ligand) in the $^{13}C\{^1H\}$ NMR spectrum (new peaks at δ 178.60, 177.18, 177.11, 75.24, 75.11, 74.89, and 74.55 ppm). Addition of *ms*-tartrate(2–) to antimony(III) (+)-tartrate(4–), on the other hand, gives no new ^{13}C NMR peaks other than single (but broadened) carboxyl and carbinol resonances which are attributable to free meso ligand. In both cases, the positions of the (+)-tartrate(4–) binuclear complex ^{13}C NMR resonance positions are unchanged. That all of the new carbinol peaks in the ^{13}C spectrum of the arsenic(III) (+)-tartrate(4–)/*ms*-tartrate(2–) mixture are upfield from the carbinol peak positions determined for sodium *ms*-tartrate(2–) in the absence of complex indicates that coordinated, deprotonated hydroxyl groups are not present in the new species.[23]

Unexpectedly complex carboxyl resonance splittings are observed in the proton-coupled ^{13}C spectra of the (+)-tartrates and these can be satisfactorily duplicated by computer synthesis only

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(36) Maloy, W. L. Ph.D. Dissertation, Case Western Reserve University, 1976.
(37) Schneider, H.-J.; Weigand, E. F. *J. Am. Chem. Soc.* **1977**, *99*, 8362.
(38) Llinás, M.; Wilson, D. M.; Neilands, J. B. *J. Am. Chem. Soc.* **1977**, *99*, 3631.

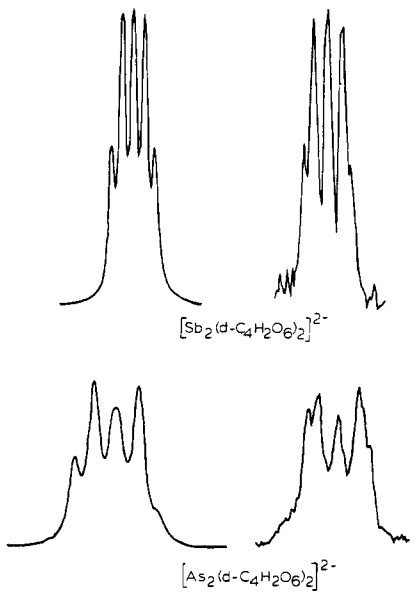

Figure 2. Observed (right) and computer-simulated (left) carboxyl multiplets observed in the ^{13}C NMR spectra of antimony(III) and arsenic(III) tartrate(4–) complexes.

by assuming coupling with three nonequivalent protons (Figure 2). The multiplets, which collapse to sharp singlets with wide-band decoupling and which remain unchanged upon substitution of H_2O solvent for D_2O, must involve protons on both bridging ligands and coupling, therefore, through at least five bonds. The presence of multiple coupling pathways and π delocalization in the coordination sphere undoubtedly enhances the long-range coupling observed here.[39]

Dimethyltartrate Complexes. (1) The three-peaked $^{13}C\{^1H\}$ NMR spectra determined for the (±)-dimethyltartrate(4–) complexes, (2) the presence of new ^{13}C resonances, whose positions and intensities are best interpreted as being due to a C_2-symmetry mixed As/Sb complex, in spectra of mixed complex salts, and (3) the equivalence of ^{13}C NMR spectra determined for active and racemic systems (Table II) demonstrate that, like the tartrate(4–) complexes, the arsenic(III) and antimony(III) dimethyltartrate(4–) species are binuclear in solution with a stability ordering *dd* (*ll*) > *dl*. Assignments for the specific resonances in the C_2 mixed As/Sb complex are based on chemical shifts and comparison with the spectrum of the mixed As/Sb tartrate species. As found for the tartrates, there are large ^{13}C NMR resonance shifts in opposite directions for the two nonequivalent carbinol carbon atoms.

There are two new and surprising observations concerning the dimethyltartrates. First, formation of the mixed As/Sb complex from the nonmixed species in D_2O is slow with a half-life of several hours (kinetic investigations are underway). Second, contrary to expectations,[1,14] a stable, crystalline 1:1 arsenic(III) *ms*-dimethyltartrate(4–) complex salt can be prepared (Table I).

An aqueous solution of the *ms*-dimethyltartrate salt exhibits a ^{13}C NMR spectrum (Table II) which appears to result from an approximately equimolar mixture of two species—one containing ligands with constitutionally similar carbon atoms which are magnetically nonequivalent (two equally intense resonances each for carboxyl, carbinol, and methyl carbons) and the other containing ligands with constitutionally similar carbons which are magnetically equivalent. The former species is almost certainly the β-$\Delta\Delta$(*ms–ms*), β-$\Lambda\Lambda$(*ms–ms*) pair of binuclear C_2-symmetry enantiomers (Figure 3) which are predicted to be the most stable of the *ms–ms* isomers[14] and which have been identified for some chromium(III) *ms*-tartrate complexes.[15] This assignment is based on (1) the large downfield shifts relative to the free *ms*-dimethyltartrate(2–) ligand of the carbinol ^{13}C NMR resonances indicative of hydroxyl group deprotonation and coordination

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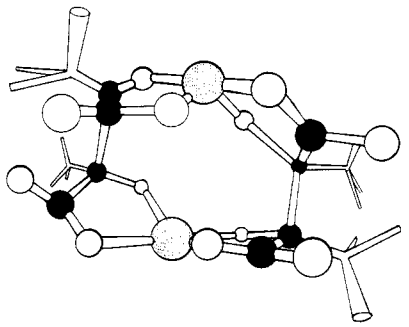
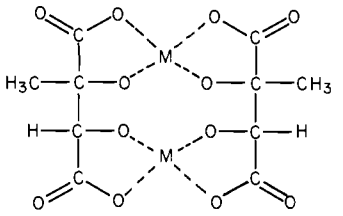


Figure 3. C_2-symmetry β-$\Delta\Delta$(*ms–ms*) isomer.

(compare with the binuclear (+)-tartrates and (±)-dimethyltartrates) and (2) the upfield shifts relative to the free ligand of the methyl carbon resonances which likely result from sterically congested methyl groups[33]—the predicted dihedral angle for a β(*ms–ms*) isomer having a pseudo-trigonal-bipyramidal coordination geometry is only 28°.[14]

The ^{13}C NMR chemical shift of the carbinol carbon indicates that the second species in $Na_2[As_2(ms\text{-}C_6H_6O_6)_2]$ solution is also coordinated to arsenic through deprotonated hydroxyl groups; however, the complex is very unlikely to be binuclear. Binuclear *ms–ms* isomers other than the β-(*ms–ms*) pair should have even smaller ligand dihedral angles (hence a larger upfield shift for the methyl group resonance—a shift not observed here (Table III)) and are expected to be significantly strained.[14] The second species is likely a monomeric complex—possibly fluxional—resulting from partial dissocation of the β-(*ms–ms*) dimer, which should be less stable than the active dimethyltartrate(4–) dimer owing to its less staggered bridging ligands.

Monomethyltartrate Complexes. The ^{13}C NMR spectra of the arsenic(III) and antimony(III) (±)-*threo*-monomethyltartrate(4–) salts are consistent with binuclear structures as found for the tartrates and dimethyltartrates. Proximal-methyl (**2**) and distal-methyl (**3**) isomers, expected to differ little in energy, are



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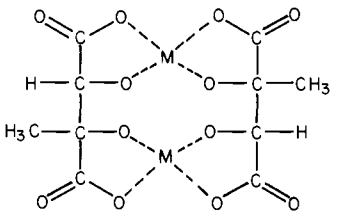

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possible for monomethyltartrate-bridged complexes. That each $^{13}C\{^1H\}$ NMR resonance of the *threo*-monomethyltartrates exhibits a slight splitting to give two equally intense peaks (except for accidental overlap in the methyl resonance of the antimony complex) shows the presence of both isomers in equal abundance.

^{13}C NMR spectral changes which occur upon mixing arsenic(III) and antimony(III) (±)-*threo*-monomethyltartrate(4–) solutions show the formation of mixed As/Sb species; however, owing to the presence of four nonmixed isomers and three mixed As/Sb isomers (two of C_2 symmetry with proximal methyl groups and one of C_1 symmetry with distal methyl groups), the spectra are extremely complex with many resonances overlapped and a detailed analysis is not feasible. Similarly, spectra of the arsenic(III) *erythro*-monomethyltartrate system are too complex for fruitful analysis, again owing to the low symmetry of the monomethyltartrate ligand. ^{13}C NMR resonance positions of the mixed

As/Sb *threo*-monomethyltartrate(4-) and arsenic(III) *erythro*-monomethyltartrate systems are not reported here.

Conclusions

These studies are the first to demonstrate conclusively the presence of binuclear species as the principal constituents of aqueous solutions of antimony(III) and arsenic(III) tartrate(4-).[40] The (±)-dimethyltartrate(4-) and *threo*-monomethyltartrate(4-) complexes have been prepared and have also been shown to be dimeric. Evidence for binuclear structures includes (1) the observation of ^{13}C NMR spectra of mixed As/Sb complexes, (2) observed long-range $^{13}C-^{1}H$ coupling involving carbon and hydrogen atoms on separate ligands in the 2:2 species, and (3) the detection of both proximal-methyl and distal-methyl isomers of the monomethyltartrate(4-)-bridged complexes. The predicted[14] stability ordering *dd* (*ll*) > *dl* has been confirmed for these binuclear complexes. The chemical-shift changes accompanying formation of the mixed As/Sb complexes provide additional evidence that bond-angle changes are involved in steric ^{13}C NMR γ effects.[31] The long-range $^{13}C-^{1}H$ couplings observed for the tartrate(4-) complexes are probably due to multiple coupling pathways as a result of the polynuclear/polydentate ligand system.

Solid 1:1 complexes of arsenic(III) with *ms*-dimethyltartrate(4-) and *erythro*-monomethyltartrate(4-) have been prepared as the sodium salts. ^{13}C NMR spectra indicate that a principal (but not the only) species in aqueous solutions of the *ms*-dimethyltartrate salt is the binuclear β-$\Delta\Delta$(*ms*-*ms*), β-$\Lambda\Lambda$(*ms*-*ms*) pair of enantiomers. That these isomers have one of the two ionized hydroxyl oxygen atoms in each ligand in an axial coordination to the trigonal-bipyramidal arsenic atom may help stabilize these species. Arsenic(III) with its d^{10} electron configuration should prefer axial coordination by good π donors.[41] Some complexation of *ms*-tartrate with arsenic(III) has also been demonstrated. Complexation of antimony(III) with meso or erythro ligands, on the other hand, apparently takes place much less readily.

Extremely slow metal ion exchange kinetics have been observed in the formation of the mixed As/Sb (±)-dimethyltartrate(4-) complex and investigations are in progress.

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(40) Potassium antimony(III) tartrate(4-) ("tartar emetic") exhibits an aqueous solution ^{13}C NMR spectrum similar to that of the sodium salt except for a small downfield shift of the two resonances (δ 183.71, 78.84 ppm). Sodium salts were used in these studies owing to their large solubilities. The chemical-shift differences between the potassium and sodium salts may be due to a small difference in the solution pH.[36]

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Soft X-ray Absorption Spectroscopy. Electronic and Morphological Structure of Poly(vinylidene fluoride)

R. S. Williams,[1a] D. Denley,[1a] D. A. Shirley,*[1a] and J. Stöhr[1b]

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720, and the Stanford Synchrotron Radiation Laboratory, Stanford, California 94305.
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Abstract: X-ray absorption studies were carried out for the first time on a polymeric thin film in the energy range 250–1000 eV, thereby providing access to the K edges of light elements. The carbon and fluorine K edges were studied in poly(vinylidene fluoride). Sharp peaks were observed at both edges, and extended fine structure (EXAFS) was found at higher energies. The carbon K edge showed compound structure, with a chemical shift of 3.9 eV between the C(1s) absorption energies in CH_2 and CF_2 groups. This type of shift is similar to, but not identical with, ESCA shifts. Fourier transformation of EXAFS structure above the F K edge yielded a C–F bond distance of 1.38 ± 0.02 Å and a second peak at 2.45 ± 0.08 Å, which is comprised of contributions from several neighbor shells, providing evidence of structural order. This method is concluded to be useful in studying polymeric electronic structure and molecular conformation.

I. Introduction

The increasing use of specialty polymers in the photographic and electronic industries has stimulated recent interest in their electronic properties.[2a] Among the most common experimental techniques employed to study polymer valence and conduction bands are X-ray and ultraviolet photoemission (XPS and UPS) and ultraviolet absorption (UVA) spectroscopies. These techniques yield complementary data, by probing both the occupied and vacant electronic states of a material for comparison with theoretical models. In addition to valence-band studies, XPS provides chemical-state information about each atomic species in a compound via chemical shifts in core-level binding energies.

To explore the electronic structure of polymers most effectively, both multitechnique analysis and theoretical understanding of the material studied are required. This paper presents the first utilization of soft X-ray absorption (SXAS) spectroscopy to study a thin-film polymer; the particular material studied was an ca. 5000 Å thick sample of poly(vinylidene fluoride) (PVF_2), an industrially important polymer[2b] (chemical formula $(CH_2CF_2)_n$). The results underscore several weaknesses of the above-mentioned spectroscopic techniques as applied to the study of polymers, and show that information obtained from SXAS data on the electronic and morphological properties of PVF_2 is indeed complementary to that obtained from electron spectroscopies, UVA, and even X-ray diffraction studies.

Section II presents a general discussion of several spectroscopic techniques which can elucidate polymer electronic structure. The

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