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Stereochemistry of Arsenic(III) and Antimony(III) 1,2-Dihydroxycyclohexane-1,2-dicarboxylates

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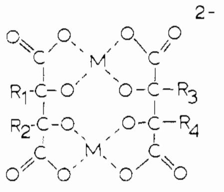
Solid salts of complexes of arsenic(III) and antimony(III) with (±)- and *meso*-1,2-dihydroxycyclohexane-1,2-dicarboxylate(4−) (dhcdc) having the general formulas $Na_2[M_2(C_8H_8O_6)_2]\cdot xH_2O$ have been prepared and characterized. ^{13}C NMR spectroscopy shows that, with the probable exception of the arsenic(III) *ms*-dhcdc complex, the complexes are binuclear in solution though the arsenic(III) (±)-dhcdc species is extensively dissociated. The presence of a well-defined β-ΔΔ(*RS*,*RS*) and β-ΛΛ(*RS*,*RS*) enantiomeric pair of C_2-symmetry isomers for the antimony(III) *ms*-dhcdc complex in aqueous solution is indicated by ^{13}C NMR spectroscopy. The crystal structure of $Na_2[As_2((\pm)\text{-}C_8H_8O_6)_2]\cdot 6H_2O$ ($P2_1/c$, $a = 9.128$ (2) Å, $b = 16.867$ (4) Å, $c = 16.039$ (4) Å, $\beta = 91.04$ (2)°, $Z = 4$) shows the presence of a racemic mixture of binuclear ΔΔ(*RR*,*RR*) and ΛΛ(*SS*,*SS*) isomeric complexes in the solid and shows indication of serious strain induced in the ligand by complex formation. This is the first report of complexes containing cyclic tartrate derivatives as ligands.

Introduction

A recent paper[1] reported ^{13}C NMR studies of binuclear arsenic(III) and antimony(III) dihydroxydicarboxylate(4−) complexes (**1**) in aqueous solution. Besides confirming the binuclear structures, these studies showed (1) the predicted[2] greater stability for isomeric complexes containing two bridges of the same enantiomeric form (*RR*,*RR* and *SS*,*SS*) compared to those containing bridges of opposite chirality (*RR*,*SS*), (2) the unexpected[3] existence of meso-ligand-containing binuclear complexes of arsenic(III), (3) unusually large long-range ^{13}C–^{1}H coupling constants, and (4) large ^{13}C chemical shift changes accompanying formation of the mixed As/Sb complexes—changes that may be due to bond angle deformations.



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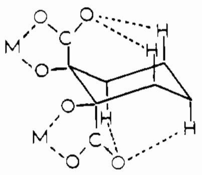
In this paper, we report synthetic, ^{13}C NMR spectroscopic, and X-ray diffraction studies of complexes of arsenic(III) and antimony(III) with 1,2-dihydroxycyclohexane-1,2-dicarboxylate (dhcdc). This ligand, which is the first cyclic tartrate derivative to be employed in complexation, is restricted in its conformational freedom compared to the acyclic tartrate derivatives studied earlier.[1] For (±)-dhcdc (the trans or *RR*,*SS* isomer), two conformers—axial, axial or *aa* and equatorial, equatorial or *ee*—are possible, while for the meso (cis or *RS*) isomer, the two possible conformers are enantiomeric and are *ae* (Figure 1). Here we have designated the conformer according to the position of the carboxyl group.

The *aa* conformer of (±)-dhcdc is expected to be less stable than the *ee* conformer from two considerations. First, axial/equatorial energy differences for hydroxyl[4] and carboxyl[5] groups allow a rough calculation of 2 kcal mol^{-1} free energy difference between the two conformers if the substituents are unionized and experience no mutual nonbonded interactions. Second, X-ray structure results for the related (±)-1,2-cyclohexanedicarboxylic acid show only *ee* structures.[6,7] However, it is precisely the higher energy *aa* conformer that is required for bridging in binuclear structures containing (±)-dhcdc. Moreover, molecular models indicate that, in such a complex, the axial carboxyl groups will be turned such that carboxyl oxygen atoms are in close contact with syn axial hydrogen atoms—a distinctly unfavorable conformation (**2**).[8]



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On the other hand, the meso isomer would bridge by precisely those conformers found for the free ligand. Thus we might expect a destabilization of the complex formed by the racemic ligand and, possibly, a stabilization of the complex formed by the meso ligand. Indeed, work with vanadyl(IV) has already shown that (±)-dhcdc is unusual in its behavior in apparently complex formation in that, though a binuclear complex can be obtained, it cannot be deprotonated completely to give a tetranegative anionic species.[9] This behavior is unlike that found for any other vanadyl(IV) dihydroxydicarboxylate investigated to date.[10]

Experimental Section

1,2-Dihydroxycyclohexane-1,2-dicarboxylic Acids. The crude mixture of isomeric ligands was prepared by hydrolysis of the cyanohydrins of 1,2-cyclohexanedione following the procedures of Tatsumi et al.;[11] however, to avoid the ester preparation and distillation employed previously, we used repeated precipitations and dissolutions of the barium salts for product purification. In addition, barium salts rather than calcium salts were employed for the isomer separations. The former proved easier to work with. These modifications are described below.

The orange-brown hydrolysate obtained by hydrolysis of the cyanohydrins prepared[11] from 25 g of 1,2-cyclohexanedione was suction filtered to remove tars and large dark crystals, was made basic (pH ~10) with 15 M NH_4OH, at which time the solution (volume, ~1

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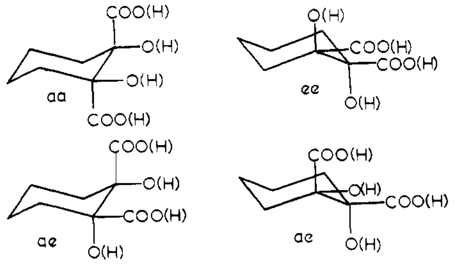

Figure 1. Conformers of 1,2-dihydroxycyclohexane-1,2-dicarboxylic acid and its anions. The trans *S,S* diastereomer is shown at the top, and the cis *R,S* (meso) diastereomer, at the bottom.

L) became turbid, and was decolorized with charcoal. To the clear yellow filtrate was added a solution of 55 g of $BaCl_2\cdot 2H_2O$ dissolved in 300 mL of H_2O. The mixture was stirred for 2 h, and the creamy white precipitate of the barium salt of dhcdc was collected by suction filtration and washed with hot water. The wet precipitate was slurried with 100 mL of water, and 12 M HCl was added dropwise while it was heated on a steam bath to effect dissolution. The yellow-brown solution was filtered and made basic (pH 10) with NH_4OH, and additional $BaCl_2\cdot 2H_2O$ solution (1 g in 5 mL of water) was added. After being stirred for 5 min, the precipitate was collected, washed with hot water, and subjected to this dissolution/precipitation process twice more. The final filtered precipitate was washed with hot water and diethyl ether and was dried with suction for 12 h to give 25.5 g of a white powder. Anal. Calcd for $BaC_8H_{10}O_6\cdot 1^1/_2H_2O$: C, 26.22; H, 3.58; Ba, 37.47. Found: C, 26.31; H, 3.56; Ba, 37.00.

For the separation of the meso and racemic forms, a slurry of 10.0 g of the barium salts in 500 mL of water was treated with 12 M HCl, added dropwise with stirring, to effect dissolution (final volume, 550 mL). Upon adjustment of the pH to ~4.3 with 15 M NH_4OH, immediate precipitation of the crude barium salt of the meso isomer occurred. The precipitate was collected, washed with hot water and diethyl ether, and suction dried to give 3.6 g of white powder. The filtrate was retained for isolation of the racemic compound.

Since the IR spectrum indicated a slight contamination by racemic material, the barium salt of *ms*-dhcdc was slurried with 250 mL of water and allowed to react with 50 mL of 12 M HCl while it was heated and stirred. The solution was filtered and titrated to pH 3.9 with 60 mL of 15 M NH_4OH to give an immediate precipitate of the pure meso salt. The product was collected, washed with diethyl ether, and dried with suction to give 1.7 g of white powder. Anal. Calcd for $BaC_8H_{10}O_6\cdot 1^1/_2H_2O$: C, 26.22; H, 3.58; Ba, 37.47. Found: C, 26.01; H, 3.60; Ba, 37.21. IR (KBr) peaks characteristic of Ba(*ms*-dhcdc): 1002, 1128, 1257 cm^{-1}.

The racemic material was isolated from the pH 4.3 filtrate from which the crude barium salt of the meso isomer was obtained. The filtrate was made basic to pH 10 with 15 M NH_4OH, and the barium salt of the racemic isomer precipitated immediately and was collected after the volume had been reduced to 100 mL on a rotary evaporator. The product was washed with hot water, dissolved in 25 mL of water with dropwise addition of 12 M HCl, and reprecipitated from the filtered solution by addition of 15 M NH_4OH to give pH 10. The barium salt of the racemic ligand (with slight contamination by the meso compound) was collected, washed with hot water and diethyl ether, and dried with suction to give 3.5 g of white powder. Anal. Calcd for $BaC_8H_{10}O_6\cdot 1^1/_2H_2O$: C, 26.22; H, 3.58; Ba, 37.47. Found: C, 24.74; H, 3.69; Ba, 37.10. IR (KBr) peak characteristic of the racemic compound: 1109 cm^{-1}.

The free acids were prepared by dissolution of the barium salts in 1 M HCl, evaporation of the solution to dryness on a rotary evaporator, and extraction of the residue with acetone. Reduction in volume of the combined acetone extracts and addition of a mixture of ligroin and CCl_4 precipitated the acids, which were recrystallized from hot glacial acetic acid. Satisfactory elemental analyses were obtained, and the melting points were in excellent agreement with literature values.[5] The ^{13}C NMR band positions are reported in Table III. IR (KBr): peaks characteristic of (±)-$C_8H_{12}O_6$ 702, 743, 910, 978, 1062 cm^{-1}; peaks characteristic of *ms*-$C_8H_{12}O_6$ 751, 800, 962, 1091, 1151 cm^{-1}.

Disodium salts of the 1,2-dihydroxycyclohexane-1,2-dicarboxylic acid isomers were prepared by evaporation of aqueous solutions of the appropriate acid neutralized with NaOH. Anal. Calcd for (±)-$Na_2C_8H_{10}O_6\cdot H_2O$: C, 36.10; H, 4.54. Found: C, 36.63; H, 4.28. IR (KBr): peaks characteristic of the racemic salt 899, 1025, 1073, 1174 cm^{-1}. Anal. Calcd for *ms*-$Na_2C_8H_{10}O_6$: C, 38.44; H, 4.06. Found: C, 38.44; H, 4.20. IR (KBr): peaks characteristic of the meso salt 659, 931, 1095, 1138 cm^{-1}.

Sodium (1,2-Dihydroxycyclohexane-1,2-dicarboxylato)arsenate(III) and -antimonate(III). All of the complex salts prepared lost water easily to give variable degrees of hydration depending on how the compounds were dried. The analyses given are for the product with only short drying times under ambient conditions and presumably reflect the degree of hydration as initially obtained. Anhydrous compounds could not be obtained without decomposition. The complex salts exhibited significant temperature dependencies of solubility in water, and recrystallizations from this solvent were easily effected. Recrystallizations from ethanol/water mixtures often gave products containing variable amounts of ethanol so that this technique was generally not used.

Sodium salts of the arsenic(III) complex were prepared by mixing cooled aqueous solutions of sodium arsenite, $NaAsO_2$, and the appropriate 1,2-dihydroxycyclohexane-1,2-dicarboxylic acid in a 1:1 mole ratio (*caution*! exothermic reaction), filtering the solution, allowing the solvent to evaporate, and collecting the crystals. Anal. Calcd for $Na_2[As_2((\pm)\text{-}C_8H_8O_6)_2]\cdot 6H_2O$: C, 27.29; H, 4.06. Found: C, 27.40; H, 4.06. Calcd for $Na_2[As_2(ms\text{-}C_8H_8O_6)_2]\cdot 5^1/_2H_2O$: C, 27.65; H, 3.91. Found: C, 27.78; H, 3.86. Drying in vacuo for 1–3 days at 65–80 °C and for 4 days at 150 °C gave complex salts prepared from the racemic ligand that were found to agree very well with analyses as a 4-hydrate and as a 2-hydrate, respectively. The salt prepared from the meso ligand reproducibly gave a 5-hydrate upon further drying under ambient conditions.

Sodium salts of the antimony(III) complexes were prepared from antimony(III) oxide, Sb_2O_3, and the appropriate 1,2-dihydroxycyclohexane-1,2-dicarboxylic acid with the procedure described elsewhere for other dihydroxydicarboxylate complexes,[1] except that ethanol was not used for the isolations of the solids. Two to four days of heating and an excess (~25%) of Sb_2O_3 were required for the best yields. The excess Sb_2O_3 was removed by filtration. Anal. Calcd for $Na_2[Sb_2((\pm)\text{-}C_8H_8O_6)_2]\cdot 5H_2O$: C, 24.64; H, 3.36. Found: C, 24.25; H, 3.17. Calcd for $Na_2[Sb_2(ms\text{-}C_8H_8O_6)_2]\cdot 7H_2O$: C, 23.56; H, 3.71. Found: C, 23.77; H, 3.84.

Physical Measurements. Natural-abundance ^{13}C NMR spectra were recorded at ca. 40 °C on a Varian FT-80 NMR spectrometer with an observation frequency of 20.0 MHz. ^{13}C NMR spectra of the free ligands were obtained with use of a 5000-Hz sweep width, 0.8-s acquisition time, 10-μs pulse width (50° pulse), and a 0.5-s pulse delay. Spectra of the complexes were obtained with use of a 500-Hz sweep width, 1.1-s acquisition time, 7-μs pulse width (40° pulse), and no pulse delay. For the NMR samples, material was dissolved in 2.0 mL of D_2O and placed in a 10-mm sample tube. Tetramethylsilane was used as an external standard in a coaxial 5-mm tube.

Crystal Structure Determination. A single crystal of $Na_2[As_2((\pm)\text{-}C_8H_8O_6)_2]\cdot 6H_2O$ was grown by cooling a solution of the compound in ethanol/water and was mounted in a glass capillary. Precession photographs established the space group as monoclinic, $P2_1/c$, with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. Diffraction data were collected on a Syntex P3/F diffractometer system at ambient temperature (~23 °C) and were treated for Lorentz and polarization effects. An empirical absorption correction based on ψ scans was applied. The crystal and data collection parameters are tabulated in Table I. Neutral-atom scattering factors and anomalous dispersion corrections were used for all atoms during the refinements.[12]

An origin-removed, sharpened Patterson map was interpreted for two trial arsenic atom positions. From Fourier maps, phased initially on these arsenic atom positions, and difference Fourier maps, the positions of all nonhydrogen atoms were obtained. Refinement of these atom positions using isotropic thermal parameters converged at $R = 10\%$. The ring hydrogen atoms were calculated in idealized positions, and their isotropic thermal parameters were set at 1.2 times the isotropic thermal parameter of their parent carbon atoms. Fourier

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(12) All calculations and plots were done with the SHELXTL 79 package: Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1979. SHELXTL uses scattering factor data compiled in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. IV, pp 55, 99, 149.

Table I. Summary of Crystal and Data Collection Parameters for $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$

fw	617.3
F_{000}	1424
a, Å	9.128 (2)
b, Å	16.867 (4)
c, Å	16.039 (4)
β, deg	91.04 (2)
V, Å^3	2469 (2)
Z	4
ρ(calcd), g cm^{-3}	1.89
space group	$P2_1/c$
cryst dimens, mm	0.2 × 0.35 × 0.55
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
abs coeff, μ(Mo Kα), cm^{-1}	29.9
scan speed, deg min^{-1}	variable, 4.0–30.0
scan range	1.0° below 2θ (Kα_1) to 1.3° above 2θ (Kα_2)
2θ limits, deg	1.0–60.0
bkgd counting time	0.5 × (scan time)
stds monitored	2 stds every 94 reflctns
reflctns collected	7891
unique reflctns	7234
m, unique data used	5085 with $F^2 > 2\sigma(F^2)$[a]
n, no. of variables refined	344
$\mathrm{ERF} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	1.14
w^{-1}	$\sigma^2(F_o) + (gF_o)^2, g = 0.032$
$R(F) = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.045
$R_w(F) = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.047
$R(F)$ including all data	0.070
x, extinction parameter in $F = F_o(1 - 10^{-4}xF_o^2/\sin\theta)$	0.00012

[a] Six bad reflections (11,2,10; 11,3,−6; 11,3,0; 11,3,3; 11,3,9; 11,4,−5) were deleted.

Table II. Fractional Coordinates for Nonhydrogen Atoms in $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$

atom	x	y	z
As(1)	0.44050 (4)	0.19727 (2)	0.35729 (2)
As(2)	0.08322 (4)	0.29743 (2)	0.16548 (2)
Na(1)	0.7414 (2)	0.4419 (1)	0.4521 (1)
Na(2)	0.3205 (2)	0.3416 (1)	0.5510 (1)
O(1)	0.3018 (3)	0.2476 (2)	0.4368 (2)
O(2)	0.0661 (3)	0.2541 (2)	0.4657 (2)
O(3)	0.2791 (3)	0.1481 (1)	0.3187 (2)
O(4)	0.0602 (3)	0.2688 (1)	0.2728 (1)
O(5)	0.0726 (3)	0.1778 (2)	0.1460 (2)
O(6)	0.0502 (4)	0.0647 (2)	0.2152 (2)
O(7)	0.5232 (3)	0.1638 (1)	0.2467 (2)
O(8)	0.5689 (3)	0.2099 (2)	0.1206 (2)
O(9)	0.4343 (3)	0.2932 (2)	0.3082 (2)
O(10)	0.2750 (3)	0.2812 (1)	0.1466 (2)
O(11)	0.1528 (3)	0.3981 (2)	0.2161 (2)
O(12)	0.3583 (4)	0.4592 (2)	0.2562 (2)
OW(1)	0.4738 (3)	0.4096 (2)	0.4450 (2)
OW(2)	0.1327 (3)	0.4368 (2)	0.5145 (2)
OW(3)	0.3055 (4)	0.5506 (2)	0.3980 (2)
OW(4)	0.2324 (4)	0.6943 (2)	0.5168 (2)
OW(5)	0.0426 (3)	0.5838 (2)	0.6329 (2)
OW(6)	0.3470 (3)	0.4568 (2)	0.6516 (2)
C(1)	0.1651 (4)	0.2267 (2)	0.4252 (2)
C(2)	0.1439 (4)	0.1610 (2)	0.3599 (2)
C(3)	0.0307 (4)	0.1874 (2)	0.2918 (2)
C(4)	0.0529 (4)	0.1374 (2)	0.2131 (2)
C(5)	0.5323 (4)	0.2202 (2)	0.1932 (2)
C(6)	0.4955 (4)	0.3029 (2)	0.2273 (2)
C(7)	0.3764 (4)	0.3422 (2)	0.1712 (2)
C(8)	0.2944 (4)	0.4054 (2)	0.2204 (2)
C(9)	0.0986 (4)	0.0842 (2)	0.4040 (3)
C(10)	−0.0594 (4)	0.0838 (3)	0.4327 (3)
C(11)	−0.1641 (4)	0.1002 (2)	0.3600 (3)
C(12)	−0.1289 (4)	0.1794 (2)	0.3189 (2)
C(13)	0.6346 (4)	0.3535 (2)	0.2358 (2)
C(14)	0.6917 (5)	0.3850 (3)	0.1530 (3)
C(15)	0.5742 (5)	0.4318 (3)	0.1069 (3)
C(16)	0.4384 (4)	0.3799 (2)	0.0917 (2)

difference maps determined after anisotropic refinement of all nonhydrogen atoms yielded reasonable positions for the water molecule hydrogen atoms. These were included in the final refinement with positions fixed at those found in the difference maps and with a common invariant isotropic thermal parameter of $U = 0.05$. A final difference map showed the highest four peaks, which were all less than 0.9 Å from the arsenic atoms, to correspond to electron densities of 0.90–0.52 e Å^{-3}. The remaining peak heights were less than 0.43 e Å^{-3}. Final agreement factors are tabulated in Table I, and the final fractional coordinates are listed in Table II. Tables of anisotropic thermal parameters, hydrogen atom parameters, hydrogen bonding distances and angles, sodium ion coordination geometries, best planes, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Ligand Stereochemistry. Chemical shifts obtained from aqueous solution ^{13}C NMR spectra of the diastereomeric forms of dhcdc, both as the free acids and as the dinegative anions, are presented in Table III. Here we use these data to support our earlier prediction that the lowest energy conformer of the racemic isomer of dhcdc is *ee* (remember that this designation gives the positions of the carboxyl groups only).

^{13}C NMR spectral data that have been reported for 1,2-cyclohexanedicarboxylic acid[13] show carboxyl, β-CH_2, and γ-CH_2 chemical shifts which are at, respectively, 1.2, 2.6, and 1.4 ppm higher field for the conformationally averaged meso diastereomer than for the racemic. Shifts to higher field for these carbon resonances are precisely what is expected if the racemic isomer is *ee* and if the axial carboxyl group of the (meso) *ae* conformer gives rise to a γ steric shift owing to 1,3-diaxial interactions with methylene groups.[14] The ^{13}C NMR spectra of the diastereomers of dhcdc, on the other hand, show (Table III) methylene resonance position differences between the meso and racemic isomers that are reversed from those found for 1,2-cyclohexanedicarboxylic acid. The meso isomer resonances are downfield from those of the racemic species. Though this might seem to indicate a conformational difference between 1,2-cyclohexanedicarboxylic acid diasteromers and their 1,2-dihydroxy derivatives, in fact it is what would be predicted. An *ae* conformer for *ms*-dhcdc will have one axial carboxyl group and one axial hydroxyl group. On the other hand, an *ee* conformer of (±)-dhcdc will have two axial hydroxyl groups. Thus, the methylene resonances of the racemic isomer are expected to occur at higher field than those of the conformationally averaged meso isomer if axial hydroxyl groups give rise to larger γ shifts than do axial carboxyl groups, and this is believed to be the case. Not only are axial hydroxyl groups in cyclohexanols known to give large upfield shifts to γ methylene carbons[16] but hydroxyl groups are also known to give upfield γ shifts in general acyclic compounds that are about 1.7 ppm larger than those found for methyl groups[16] (which are comparable to carboxyl groups[17,18]). Moreover, the carboxyl resonance of *ms*-dhcdc is upfield from that of the racemic diastereomer. This is the same ordering as found for 1,2-cyclohexanedicarboxylic acid[13] and is the ordering expected for an upfield γ effect on the more axial carboxyl groups of the meso diastereomers. Finally, we

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[14] Though the origin of "steric" γ shifts is highly controversial, there is no doubt that a generalized heteroatom γ effect has been found experimentally for a variety of substituents.[15]

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Table III. ^{13}C NMR Chemical Shifts for Isomers of 1,2-Dihydroxycyclohexane-1,2-dicarboxylic Acid and Its Compounds

		δ [amplitude][a]			
compd	concn, M	-COO(H)	>CO(H)	β-CH_2	γ-CH_2
(±)-$C_8H_{12}O_6$	1.0	178.85 [1.0]	77.57 [1.3]	31.82 [2.9]	20.39 [3.2]
ms-$C_8H_{12}O_6$	1.0	177.89 [1.0]	78.42 [1.3]	33.28 [5.6]	21.02 [6.6]
Na_2((±)-$C_8H_{10}O_6$)	1.0	184.70 [1.0]	77.69 [2.2]	32.15 [2.2]	20.90 [2.1]
Na_2(*ms*-$C_8H_{10}O_6$)	1.0	181.82 [1.0]	79.81 [1.4]	33.70 [5.0]	22.32 [6.3]
Na_2{As_2((±)-$C_8H_8O_6$)$_2$]	0.2	181.43 [1.0]	83.97 [1.4]	36.22 [2.6]	22.30 [2.6]
			77.28 [0.5][b]	31.98 [1.3][b]	20.61 [2.8][b]
Na_2{Sb_2((±)-$C_8H_8O_6$)$_2$}	0.2	184.34 [1.0][c]	83.03 [2.0]	37.42 [6.5]	22.85 [7.5]
Na_2[As_2(*ms*-$C_8H_8O_6$)$_2$}	0.2	180.9[d]	80.1[d]	34.3[d]	21.5[c]
Na_2{Sb_2(*ms*-$C_8H_8O_6$)$_2$]	0.2	184.21 [1.0][c]	83.92 [1.4][c]	36.41 [0.8][c]	22.68 [1.1][c]
		184.07 [1.3][c]	82.42 [1.6][c]	33.62 [0.8][c]	20.20 [0.9][c]

[a] Peak height relative to that of the peak at lowest field. [b] These resonances are not assigned to the binuclear dhcdc complex. They are probably due to partially or totally dissociated ligand. [c] Slightly broadened. [d] Severely broadened (1-3 ppm at half-height); resonance center given.

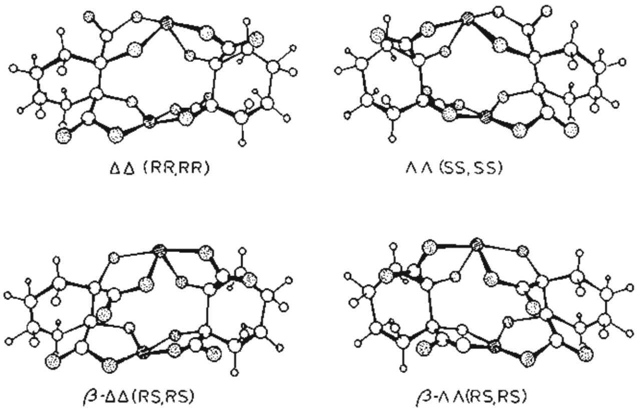

Figure 2. Isomers expected for the complexes $[M_2((\pm)\text{-dhcdc})_2]^{2-}$ and $[M_2(ms\text{-dhcdc})_2]^{2-}$, M = Sb, As.

note that ionized carboxyl groups give rise to decreased γ shifts[18] and this should lead to decreases in the chemical shift differences between corresponding methylene carbon atoms of the meso and racemic diastereomers of dhcdc upon ionization. This is precisely what is seen (Table III). All of these observations provide strong evidence for our conclusion of an *ee* preferred conformer for free (±)-dhcdc.

^{13}C NMR Spectra of Complexes. The isomers expected for binuclear complexes containing metal ions with pseudo-trigonal-bipyramidal coordination geometries (as found in the arsenic(III)[19] and antimony(III)[3] tartrates) are the enantiomeric pairs ΔΔ(*RR*,*RR*), ΛΛ(*SS*,*SS*) for the racemic system and β-ΔΔ(*RS*,*RS*), β-ΛΛ(*RS*,*RS*) for the meso (Figure 2).[2,20] The former pair should have D_2 symmetry with four ^{13}C NMR resonances expected—one each from carboxyl, carbinol, and two types of methylene carbon atoms (β and γ to the carboxyl groups). The latter pair of isomers is expected to have C_2 symmetry with two resonances for each type of carbon atom (eight resonances total).

The spectra predicted are precisely those observed for the antimony(III) complexes (Table III). In these complexes, the large downfield shifts of the carbinol resonances upon complexation show conclusively ionization and coordination of the hydroxyl groups,[1,21,22] as expected. The downfield shifts of the methylene carbon resonances in the coordinated racemic ligand compared to those of the free ligand are undoubtedly due to a decreased γ perturbation since the more perturbing hydroxyl groups must be equatorial in the ΔΔ(*RR*,*RR*), ΛΛ-(*SS*,*SS*) complexes. Interestingly, the antimony(III) β-ΔΔ-(*RS*,*RS*), β-ΛΛ(*RS*,*RS*) complex shows one β-CH_2 resonance (36.41 ppm) and one γ-CH_2 resonance (36.41 ppm) which are very close to those determined for the (±)-dhcdc complex. These resonances must correspond to methylene groups γ to the axial carboxyl group. The other methylene resonances (33.62, 20.20 ppm) of the *RS*,*RS* isomers are upfield and correspond to methylene groups γ to the axial hydroxyl group. Note that, in the coordinated *ms*-dhcdc ligand, conformational averaging does not occur to give NMR equivalency to carbon atoms of the same type (i.e., same connectivity), as is the case with the free ligand. The absence of any peaks attributable to a coexisting isomer in solution indicates the instability of binuclear complexes with bridging ligands of opposite chirality, *RR*,*SS*, relative to that of the *RR*,*RR* and *SS*,*SS* species.[1]

The ^{13}C NMR spectra of the arsenic(III) complexes (Table III) are not as simple as those of the antimony(III) complexes. In the spectrum of the arsenic(III) complex of (±)-dhcdc, in addition to peaks at 181.43, 83.97, 36.22, and 22.30 ppm, which we attribute to binuclear ΔΔ(*RR*,*RR*), ΛΛ(*SS*,*SS*) complexes, extra resonances are found. Similar additional resonances are observed in spectra of arsenic(III) tartrates and substituted tartrates.[1] If one extra resonance peak is overlapped with the peak at 181.43 ppm, all of the extra resonances except for that due to the carbinol carbon at 77.28 ppm lie between those found for the free racemic acid and its sodium salt. These extra peaks are likely due to ligands that are free or only loosely associated with arsenic(III) owing to total or partial dissociation of the complexes. That the peaks seem to lie between those of the salt and those of the free acid is not unexpected since the solutions are relatively acidic (apparently owing to formation of moderately soluble $As(OH)_3$ from relatively acidic and unstable[23] cationic arsenic(III) species formed initially upon complex dissociation). The intensities of the extra peaks are much higher (relative to those attributed to the binuclear anionic complex) than those found for the arsenic(III) tartrates and substituted tartrates.[1] This indicates a much greater dissociation for the arsenic (±)-dhcdc complex, not an unexpected observation since the ligand is known to be in an unfavorable conformation. Apparently the antimony(III) (±)-dhcdc complex has such a sufficiently increased stability (relative to that of dissociated species) that no dissociation is detected. Since the ^{13}C spectrum of the arsenic(III) (±)-dhcdc complex is complicated by additional resonances, a crystal structure of the sodium salt has been carried out both to confirm the binuclear structure and isom-

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Table IV. Interatomic Distances and Angles for $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$ with Estimated Standard Deviations in Parentheses

Distances, Å			
As(1)-As(2)	4.753 (1)	C(2)-O(3)	1.427 (4)
As(1)-O(1)	2.002 (3)	C(3)-O(4)	1.433 (4)
As(1)-O(7)	2.021 (3)	C(6)-O(9)	1.431 (4)
As(2)-O(5)	2.044 (3)	C(7)-O(10)	1.434 (4)
As(2)-O(11)	1.981 (3)	C(1)-C(2)	1.534 (5)
As(1)-O(3)	1.792 (2)	C(3)-C(4)	1.534 (5)
As(1)-O(9)	1.800 (2)	C(5)-C(6)	1.538 (5)
As(2)-O(4)	1.803 (2)	C(7)-C(8)	1.529 (5)
As(2)-O(10)	1.803 (2)	C(2)-C(3)	1.555 (5)
C(1)-O(1)	1.306 (4)	C(6)-C(7)	1.548 (5)
C(4)-O(5)	1.289 (5)	C(2)-C(9)	1.536 (5)
C(5)-O(7)	1.284 (4)	C(3)-C(12)	1.534 (5)
C(8)-O(11)	1.299 (5)	C(6)-C(13)	1.534 (5)
C(1)-O(2)	1.214 (5)	C(7)-C(16)	1.542 (5)
C(4)-O(6)	1.226 (5)	C(9)-C(10)	1.522 (6)
C(5)-O(8)	1.229 (5)	C(11)-C(12)	1.526 (5)
C(8)-O(12)	1.218 (5)	C(13)-C(14)	1.531 (6)
		C(15)-C(16)	1.533 (6)
		C(10)-C(11)	1.520 (6)
		C(14)-C(15)	1.513 (6)

Angles, Deg			
O(1)-As(1)-O(7)	158.2 (1)	C(2)-C(3)-C(12)	113.4 (3)
O(5)-As(2)-O(11)	157.3 (1)	C(3)-C(2)-C(9)	112.6 (3)
O(3)-As(1)-O(9)	104.2 (1)	C(6)-C(7)-C(16)	113.1 (3)
O(4)-As(2)-O(10)	104.5 (1)	C(7)-C(6)-C(13)	112.7 (3)
O(1)-As(1)-O(3)	83.7 (1)	C(2)-C(9)-C(10)	114.0 (3)
O(7)-As(1)-O(9)	83.9 (1)	C(3)-C(12)-C(11)	114.1 (3)
O(4)-As(2)-O(5)	82.8 (1)	C(6)-C(13)-C(14)	114.2 (3)
O(10)-As(2)-O(11)	83.9 (1)	C(7)-C(16)-C(15)	114.3 (3)
C(1)-O(1)-As(1)	114.1 (2)	C(9)-C(10)-C(11)	110.7 (3)
C(5)-O(7)-As(1)	114.2 (2)	C(10)-C(11)-C(12)	110.9 (3)
C(4)-O(5)-As(2)	113.6 (2)	C(13)-C(14)-C(15)	110.8 (3)
C(8)-O(11)-As(2)	114.5 (2)	C(14)-C(15)-C(16)	110.1 (3)
C(2)-O(3)-As(1)	118.8 (2)	O(1)-C(1)-C(2)	113.6 (3)
C(6)-O(9)-As(1)	119.3 (2)	O(5)-C(4)-C(3)	114.8 (3)
C(3)-O(4)-As(2)	119.0 (2)	O(7)-C(5)-C(6)	114.6 (3)
C(7)-O(10)-As(2)	118.0 (2)	O(11)-C(8)-C(7)	113.7 (3)
C(1)-C(2)-O(3)	109.1 (3)	O(3)-C(2)-C(3)	106.7 (3)
C(4)-C(3)-O(4)	108.9 (3)	O(4)-C(3)-C(2)	107.4 (3)
C(5)-C(6)-O(9)	108.1 (3)	O(9)-C(6)-C(7)	107.1 (3)
C(8)-C(7)-O(10)	108.8 (3)	O(10)-C(7)-C(6)	107.2 (3)

eric form and to elucidate the steric consequences of the unfavorable ligand conformation.

The chemical shift differences between the arsenic(III) and antimony(III) (±)-dhcdc complexes for carboxyl, carbinol, and β-CH_2 groups are respectively $\delta_{As} - \delta_{Sb} = -2.9$, 1.0, and −1.2 ppm. These compare very well with values of −2.9 to −3.2, 0.8–0.9, and −1.1 to −1.2 ppm determined for carboxyl, alkyl-substituted carbinol, and methyl (again, α to carbinol) groups in tartrate and methyl-substituted tartrate complexes.[1] It is interesting that the chemical shift differences between corresponding carbon atoms in arsenic(III) and antimony(III) complexes remain so constant for a relatively wide range of ligands.

The aqueous solution spectrum of the sodium salt of the arsenic *ms*-dhcdc complex is rather uninformative. With the exception of the γ-CH_2 ^{13}C NMR resonance, all of the peaks are very broad (1–3 ppm at half-height). That the positions of the midpoints are near those of the free meso ligand resonances indicates that the spectrum may arise primarily from a partially or completely dissociated ligand. The broadening may be due to exchange with a coordinated ligand. A spectrum recorded at higher temperature (90 °C) shows resonances that are slightly broader (except for the carbinol carbon resonance, which is severely broadened) but unchanged in position. Though the solution species does not appear to be a complex similar to that found for the antimony(III) *ms*-dhcdc complex, the similarities in the IR spectra of the sodium salts of the arsenic(III) and antimony(III) meso complexes leave little doubt that these salts contain identical species in the solid state.

Structure of (±)-$[As_2(C_8H_8O_6)_2]^{2-}$. A racemic mixture of ΔΔ(*RR*,*RR*) and ΛΛ(*SS*,*SS*) binuclear isomers—i.e., those isomers expected to be most stable[2,20]—is found in the structure determination. The geometry of the complex ion, which is shown in Figure 3 and whose interatomic distances and angles are listed in Table IV, resembles the structure found for bis(μ-tartrato(4−))bis(arsenate(III)),[19] $[As((+)\text{-}C_4H_2O_6)_2]^{2-}$, and for a number of antimony(III) tartrate analogues.[3,24] The coordination geometry is pseudo trigonal bipyramidal with average axial and equatorial angles of 157.8° (±0.4° average deviation) and 104.4 (2)° (**3**) (compare with 161.3 (1) and

3

102.0 (1)° for $[As_2((+)\text{-}C_4H_2O_6)_2]^{2-}$ [19] and with 150 (2) and 100 (4)° for $[Sb_2(C_4H_2O_6)_2]^{2-}$ [3]). Within the limits of ex-

Table V. Selected Torsion Angles for $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$ and Averages for Diastereomers of 1,2-Cyclohexanedicarboxylic Acid (CHDCA)

	angles, deg			
atoms	$Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$[a]	(+)-CHDCA[b]	(±)-CHDCA[c]	*ms*-CHDCA[d]
O(1)-C(1)-C(2)-O(3)	−9.0 (4)			
O(5)-C(4)-C(3)-O(4)	−8.9 (4)			
O(7)-C(5)-C(6)-O(9)	−10.3 (4)			
O(11)-C(8)-C(7)-O(10)	−11.7 (4)			
O(3)-C(2)-C(3)-O(4)	−77.1 (3)			
O(9)-C(6)-C(7)-O(10)	−78.6 (3)			
C(9)-C(2)-C(3)-C(12)	42.8 (4)	−50	−47	−55
C(13)-C(6)-C(7)-C(16)	42.8 (4)			
C(3)-C(2)-C(9)-C(10)	−48.1 (4)	53	50	54
C(2)-C(3)-C(12)-C(11)	−46.8 (4)			
C(7)-C(6)-C(13)-C(14)	−47.9 (4)			
C(6)-C(7)-C(16)-C(15)	−47.4 (4)			
C(2)-C(9)-C(10)-C(11)	55.8 (5)	−58	−57	−56
C(3)-C(12)-C(11)-C(10)	54.2 (4)			
C(6)-C(13)-C(14)-C(15)	55.9 (5)			
C(7)-C(16)-C(15)-C(14)	54.8 (5)			
C(13)-C(14)-C(15)-C(16)	−57.6 (5)	60	59	57
C(9)-C(10)-C(11)-C(12)	−57.6 (4)			

[a] Estimated standard deviations are given in parentheses. [b] Reference 7. [c] Reference 6. [d] Reference 25.

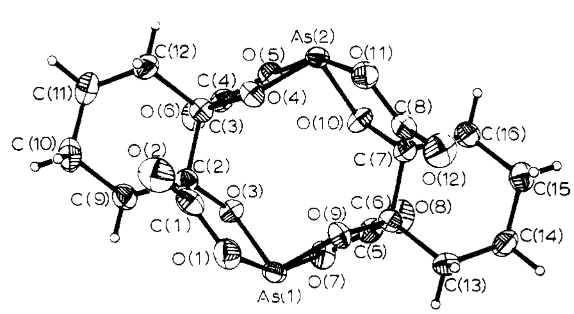

Figure 3. View of the $[As_2(C_8H_8O_6)_2]^{2-}$ anion. Thermal ellipsoids are shown at the 50% probability level (except for the hydrogen atoms).

perimental accuracy, corresponding arsenic–oxygen distances in the tartrate[19] and 1,2-dihydroxycyclohexane-1,2-dicarboxylate structures are identical.

Of great interest are the torsion angles given in Table V for the arsenic(III) (±)-dhcdc anionic complex. The values of the O–C–C–O torsion angles involving coordinated hydroxyl and carboxyl oxygen atoms—torsion angles whose nonzero values indicate small nonplanarities of the α-hydroxycarboxylate groups—are similar in magnitude to those observed for other α-hydroxycarboxylate compounds.[24] The chelate rings as a whole, however, are strikingly planar (see the supplementary material) and unexpectedly fail (with one exception among the four crystallographically independent chelate rings) to show the asymmetric envelope conformation found for most other α-hydroxycarboxylate chelates.[24] The O–C–C–O dihedral angles involving the coordinated hydroxyl oxygen atoms (average 78°) are significantly larger than those found for the arsenic(III) tartrate(4–) complex (average 64°).[19] Finally, a comparison of the torsion angles for the cyclohexane rings in the arsenic(III) (±)-dhcdc complex with those found for diastereomers of 1,2-cyclohexanedicarboxylic acid (Table V) shows a dramatic flattening of the rings in the arsenic(III) compound. This flattening is apparently due to a strong interaction between oxygen atoms of the axial carboxyl groups and axial hydrogen atoms on γ carbons. Calculations employing the observed carboxyl oxygen coordinates and the idealized methylene hydrogen atom coordinates give distances of 2.53–2.65 Å for these oxgyen–hydrogen distances (supplementary material). These distances are considerably shorter than the sum of the van der Waals radii for hydrogen (~1.5 Å)[26] and oxygen (~1.6 Å).[27] Although it has been stated that experimentation shows that the degree of flattening of cyclohexane rings is practically unaffected by axial substituents,[26] in the present case, there is no doubt that the axial carboxyl groups which are forced to point into the interior of the ring cause severe ring flattening.

Packing Geometry in $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$. A stereodrawing of the unit cell contents of the arsenic(III) complex is shown in Figure 4, and coordination angles and distances involving the sodium ions and water molecules are given in the supplementary material. The two crystallographically independent sodium ions are 6-coordinate with Na(1) coordinated to only water molecule oxygen atoms and Na(2) coordinated to three water molecule oxygen atoms and three ligand oxygen atoms (O(1), O(8), O(10)). The sodium ions and coordinated water molecules lie in columns parallel to the *a* axis and tie together columns of anions by hydrogen and ion-dipole bonding. With one exception, OW(4), all water molecules act as hydrogen donors toward two oxygen atoms and as electron-pair donors toward two sodium ions and/or water molecule hydrogen atoms. OW(4) is 3-coordinate and acts as a hydrogen atom donor toward two oxygen atoms and as an electron pair donor toward Na(1). The OW(4)–Na(1) distance is the shortest found in this structure for any sodium–oxygen contact (2.362 (4) Å). For the most part, the water molecules tie together sodium ions and ionic complexes; there are only two crystallographically distinct water–water contacts.

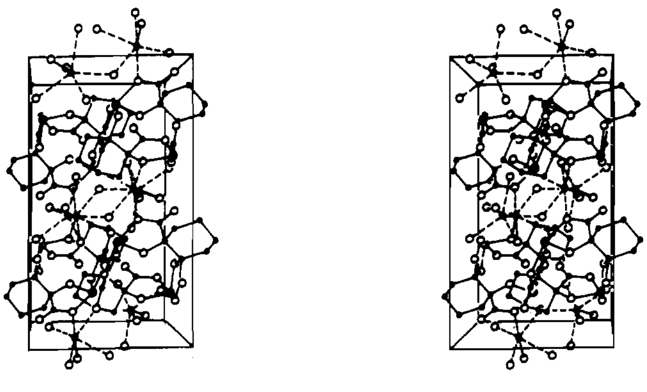

Figure 4. Stereoview of the unit cell of $Na_2[As_2(C_8H_8O_6)_2]\cdot 6H_2O$. The view is into the *ac* plane. A dot marks the origin of the right-handed coordinate system. Carbon and oxygen atoms are denoted by open circles; arsenic and sodium atoms, by crosshatching. Hydrogen atoms are not shown. Dotted lines show sodium coordination.

Conclusions

The dhcdc complexes of arsenic(III) and antimony(III) are binuclear both in the solid state and (with the probable exception of the arsenic(III) *ms*-dhcdc complex) in solution. The complexes of (±)-dhcdc appear to be significantly strained owing to an unfavorable ligand conformation. The ^{13}C NMR spectral results indicate a significantly lower stability for the arsenic(III) derivatives. No evidence is found for the presence of any binuclear *RR,SS* isomers in solutions of the (±)-dhcdc complexes, nor is there evidence for other than the single β-ΔΔ(*RS,RS*), β-ΛΛ(*RS,RS*) racemic diastereomer (among several possible[2]) in solutions of the antimony(III) *ms*-dhcdc species. Thus these complexes also exhibit the large stereoselectivity found for related systems.[1] Though complexes of tartrate and acyclic tartrate derivatives have been extensively studied,[2,3,24] this is the first report of complexation by a cyclic tartrate derivative.

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Registry No. (±)-$C_8H_{12}O_6$, 13307-15-8; *ms*-$C_8H_{12}O_6$, 13511-16-5; Na_2((±)-$C_8H_{10}O_6$), 82080-57-7; Na_2(*ms*-$C_8H_{10}O_6$), 82080-58-8; $Na_2[As_2$((±)-$C_8H_8O_6)_2]\cdot 6H_2O$, 82080-85-1; $Na_2[Sb_2$((±)-$C_8H_8O_6)_2]$, 82080-86-2; $Na_2[As_2$(*ms*-$C_8H_8O_6)_2]$, 82093-49-0; $Na_2[Sb_2$(*ms*-$C_8H_8O_6)_2]$, 82165-88-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, hydrogen bonding distances and angles, sodium ion coordination geometries, best planes, and observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.

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