Antimony(III) Complexes with Carboxylic Acids. Part 2.[1] Preparation and Crystal Structures of [Sb₂Ag₂(C₆H₆O₇)₄] and [SbNa(C₆H₆O₇)₂(H₂O)₂]·H₂O [C₆H₆O₇ = citrate(2−)]†

David W. Hartley,[a] Graham Smith,*,[a] Dalius S. Sagatys[a] and Colin H. L. Kennard[b]

[a] School of Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, 4001, Australia

[b] Department of Chemistry, The University of Queensland, Brisbane, 4072, Australia

The antimony(III)–silver(I) and –sodium(I) complexes with citric acid ($C_6H_8O_7$), [Sb₂Ag₂(C₆H₆O₇)₄] **1** and [SbNa(C₆H₆O₇)₂(H₂O)₂]·H₂O **2**, have been prepared and their crystal structures determined by X-ray diffraction and refined to residuals of $R = 0.023$ and 0.017 for 2403 and 2969 observed reflections respectively. Crystals are monoclinic, space group $P2_1/n$, and $P2_1/a$. Complex **1** has two dimers in a cell of dimensions $a = 6.557(4)$, $b = 12.149(2)$, $c = 20.50(1)$ Å and $\beta = 98.12(3)°$, while there are four monomers of **2** in a cell with $a = 14.470(5)$, $b = 7.193(3)$, $c = 18.747(6)$ Å and $\beta = 92.22(2)°$. In each structure antimony is bonded to two oxygens of two crystallographically independent citrate(2−) residues in classic pseudo-trigonal-bipyramidal antimony(III) four-co-ordination [Sb–O 2.007(2)–2.218(2), **1**; 1.988(1)–2.164(1) Å, **2**]. These oxygens are from the α-hydroxycarboxylate groups giving five-membered chelate rings. In **1** each antimony centre is in turn linked through one of these carboxylate groups to two silver(I) ions in an asymmetric bis(carboxylato-O,O') bridge [Ag–O 2.314(2) and 2.661(2) Å]. Hydroxyl groups complete the angular three-co-ordination about each silver [Ag–O 2.323(2) Å], giving a centrosymmetric cyclic dimer structure. In contrast, complex **2** is monomeric with the sodium and two co-ordinated waters [Na–Ow 2.404(2) and 2.512(2) Å] forming a tris(oxo)-bridged complex unit (two oxygens from the α-hydroxycarboxy groups), with a Na–O range of 2.413(2)–2.562(2) Å [Na · · · Sb 3.665(1) Å].

The stereochemistry of compounds of antimony(III) with oxygen donor ligands is usually based on a very distorted trigonal bipyramid with a sterically active lone pair of electrons in one of the trigonal-planar sites. Thus for three- and four-co-ordination the resulting complexes have a pyramidal (**A**) or a pseudo-trigonal-bipyramidal stereochemistry (**B**) respectively.[2]

    A   **B**

Among the few known antimony(III) carboxylates the classical bis[tartrato(4−)]-bridged dimer anion [Sb₂(C₄H₂O₆)₂]²⁻ is the best typified. This exists in essentially unchanged form in compounds with both uni- and di-valent counter ions (NH₄⁺, Na⁺, K⁺, Ca²⁺, Sr²⁺, Ba²⁺), with the cations as discrete ions. However, the silver(I) compound, having the basic formula [{Ag₄Sb₄(C₄H₂O₆)₄(H₂O)₄}ₙ], has associations which are distinctly non-ionic, with the silver forming bridges between the antimony dimers.[1] The result is a complex polymer network structure. In the only other known antimony(III) carboxylate, an unusual pentagonal-pyramidal structure results from the co-ordination of three oxalato(2−) ligands in the compound [NH₄]₃[Sb(C₂O₄)₃]·4H₂O.[3] Analogous antimony(III) citrate complexes are uncommon. In the hexaamminecobalt(III) salt of bis[citrato(3−)]antimonate(III) both cobalt and antimony are co-ordinated, with antimony having pseudo-trigonal-bipyramidal stereochemistry.[4] This co-ordination is very similar to that observed in the antimony(III) tartrates. In this light it was considered useful to consider the

effect of silver(I) stabilisation on the antimony(III) citrate system and on other hydroxy acid complexes of this metal. The first examples from this series are the silver(I) and sodium(I) complexes with antimony(III) citrate. These have the basic stoichiometry [SbAg(C₆H₆O₇)₂] **1** and [SbNa(C₆H₆O₇)₂(H₂O)₃] **2**. In each the citrate ligands were found to be dianionic.

Experimental

Preparation.—The complexes **1** and **2** were prepared by digesting at 90 °C an excess of antimony(III) oxide (2 g) with 5% aqueous citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) solution (100 cm³). The unreacted Sb₂O₃ was removed by filtration and aqueous silver or sodium nitrate (10 cm³, 1 mol dm⁻³) added to the filtrate. After concentration of this solution, colourless prismatic crystals formed in several days. Elemental analyses were consistent with [SbAg(C₆H₆O₇)₂] **1** and [SbNa(C₆H₆O₇)₂]·3H₂O **2** (Found for **1**: C, 23.0; H, 1.85. Calc. for C₁₂H₁₂AgO₁₄Sb: C, 23.6; H, 2.00. Found for **2**: C, 24.5; H, 3.10. Calc. for C₁₂H₁₈NaO₁₇Sb: C, 24.9; H, 3.15%).

Crystal Structure Determinations.—*Crystal data.* **1**, C₂₄H₂₄Ag₂O₂₈Sb₂, $M = 1219.7$, monoclinic, space group $P2_1/n$, $a = 6.557(4)$, $b = 12.149(2)$, $c = 20.50(1)$ Å, $\beta = 98.12(3)°$, $U = 1617(1)$ Å³, $D_m = 2.51$, $Z = 2$, $D_c = 2.504$ g cm⁻³, Mo-Kα radiation, $\lambda = 0.710\ 73$ Å, μ(Mo-Kα) = 29.5 cm⁻¹, $F(000) = 1176$, 296 K.

2, C₁₂H₁₈NaO₁₇Sb, $M = 579.0$, monoclinic, space group $P2_1/a$, $a = 14.470(5)$, $b = 7.193(3)$, $c = 18.747(6)$ Å, $\beta = 92.22(2)°$, $U = 1949.7(9)$ Å³, $D_m = 1.97$, $Z = 4$, $D_c = 1.971$ g cm⁻³, Mo-Kα radiation, $\lambda = 0.710\ 73$ Å, μ(Mo-Kα) = 15.5 cm⁻¹, $F(000) = 1152$, 296 K.

X-Ray diffraction data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-crystal-monochromatised Mo-Kα X-radiation. A total of 2764 for **1** and 3425
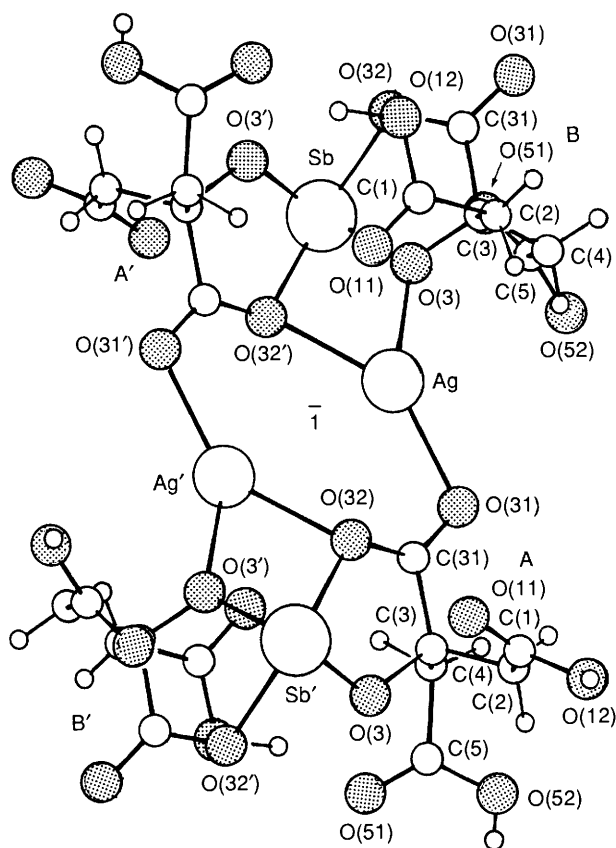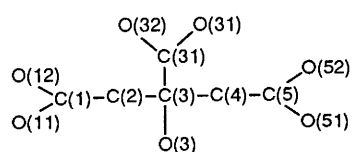

Fig. 1 Molecular configuration and atom numbering scheme for complex **1**. Primed atoms are generated by an inversion operation

for **2** unique reflections were collected from crystals with dimensions $0.35 \times 0.15 \times 0.12$ and $0.33 \times 0.15 \times 0.12$ mm respectively (collection ranges, $2\theta_{max} = 50°$; $h\,0$–7, $k\,0$–14, $l\,-24$ to $+24$ for **1** and $h\,0$–17, $k\,0$–8, $l\,-22$ to $+22$ for **2**). Of these, 2403 and 2969 with $I > 2.5\sigma(I)$ were considered observed and used in structure refinement. An overall loss of 6.4% in the intensities of three standards monitored over the 42 h of data collection for **1** indicated some crystal decay which was allowed for by scaling of data. Data were also corrected for absorption (maximum, minimum transmission factors: 100, 86, **1**: 100, 97%, **2**). The structures were determined using the automatic Patterson procedure of SHELXS 86[5] and refined by full-matrix anisotropic least squares (SHELX 76[6]) to residuals $R(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.023 for **1** and 0.017 for **2** and $R'[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ of 0.026 and 0.021. Values of $w = 1.00/(\sigma^2 F_o + 6.8 \times 10^{-4} F_o^2)$ and $0.50/(\sigma^2 F_o + 9.5 \times 10^{-4} F_o^2)$ were used for **1** and **2** respectively. Hydrogen atoms were located in Fourier-difference analyses and included in the respective refinements with both positional and thermal parameters refined. Neutral atom scattering factors were used[6] with f',f'' terms for anomalous dispersion also from ref. 7. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

The atom numbering scheme used for the citrate residues in the structures **1** and **2** is shown below.

O(32)   O(31)
 \   /
  C(31)
O(12) | O(52)
  \ | /
   C(1)—C(2)—C(3)—C(4)—C(5)
  / | \
O(11) | O(51)
        O(3)

Discussion

Complex **1**, $[Sb_2Ag_2(C_6H_6O_7)_4]$.—The structure of the antimony silver citrate complex **1** comprises discrete centrosymmetric dimeric units with formula $[\{AgSb(C_6H_6O_7)_2\}_2]$ (Fig. 1). Each antimony in the dimer is four-co-ordinate with a classical pseudo-trigonal-bipyramidal stereochemistry. The four oxygen donor atoms are from two citrate(2−) ligands, the two in axial sites from carboxylate groups [Sb–O 2.096(2) and 2.218(2) Å; O–Sb–O 137.5(1)°], those in the equatorial sites from hydroxyl groups [Sb–O 2.007(2) and 2.008(2) Å; O–Sb–O 105.2(1)°]. The stereochemically active lone pair on antimony presumably occupies the other equatorial site of the trigonal bipyramid, consistent with observations for antimony(III) complexes.[2,8] The only donor atoms involved in bonding in this complex are oxygens from the 'inner' α-hydroxycarboxyl groups [attached to C(3)], giving two crystallographically independent five-membered chelate rings, with bite angles at Sb of 76.0 and 78.1(1)°. An identical system is found with complex **2**, $[SbNa(C_6H_6O_7)_2(H_2O)_2]\cdot H_2O$. Evidence for the existence of a 2− net charge on each ligand, arising from this α-hydroxycarboxyl group rather than by deprotonation of either of the terminal carboxyl groups, is (*i*) the location of the protons on the terminal groups, (*ii*) the association of each of these groups in intermolecular hydrogen-bonding associations and (*iii*) the relative bond lengths between these oxygens and antimony. The Sb–O (hydroxyl) distances are significantly shorter [by 0.09–0.17 Å, *cf.* Sb–O(carboxyl) distances]. These values compare with the equivalent distances in the analogous antimony(III) tartrate dimer anions, $[Sb_2(C_4H_2O_6)_2]^{2-}$, in which both carboxyl and hydroxyl groups are deprotonated. In the case of D-potassium bis[tartratoantimonate(III)] trihydrate (d-tartar emetic)[9] the corresponding Sb–O distances are 1.99(1) (mean) (hydroxyl), *cf.* 2.16(1) Å (mean) (carboxyl). Furthermore, bond strengthening accompanies deprotonation of the hydroxyl group. This has been observed in bis(chelate) complexes of boron(III) with citrate(2−)[10] as well as with malate(2−).[11] Citrate complexes with antimony(III) are rare, and so far there is only one example for which crystallographic data are available, hexaamminecobalt(III) bis[citrato(3−)]antimonate(III).[4] In addition to chelation *via* both deprotonated hydroxyl and 'inner' carboxyl groups, one of the terminal groups is also deprotonated. Thus, with variations in the terminal groups, it would appear that with antimony(III) bis-chelation as observed in both complexes **1** and **2** is preferred for α-hydroxycarboxylate interactions, a contention supported by Tapscott[12] for other metal ions.

The remaining part of this dimeric structure comprises silver ions which bridge the two antimony citrate complex units. This occurs *via* an asymmetric bis(carboxylato-*O,O'*) bridge[Ag–O 2.314(2) and 2.661(2) Å; O–Ag–O 134.1(1)°], across an inversion centre in the cell. In the terminal sites are bridging hydroxyl oxygens [O(3B), Ag–O 2.323(2) Å]. All of these oxygens are from the same α-hydroxycarboxyl group involved in bonding to the antimony ions. The bis(carboxylato-*O,O'*)-bridged dimer is common among silver(I) carboxylates[13] and represents a Type 2 dimer in the classification of Mak *et al.*,[14] forming a *syn-syn* carboxylate–metal interaction. There are only two exceptions,[15] the isomorphous silver(I) complexes of 2,4-dichlorophenoxyethanoic acid and 4-chloro-2-methylphenoxyethanoic acid. They have the *anti-syn* motif. The Ag···Ag' separation in **1** is somewhat longer than is typical for silver(I) dimers [3.221(1) Å, *cf.* 2.78–2.97 Å for a series of comparable compounds].[14] This arises from the larger-than-normal asymmetry in the Ag–O bond distances which in turn reduces the O–Ag–O angle from typically[14] 156° to the observed value.

In addition to the formal bonds involving the metals, the protonated carboxyl oxygens are involved in inter-dimer hydrogen-bonding associations (Fig. 2). These are O(12A)··· O(31A) (1 + x, y, z; 2.76 Å), O(11B)···O(31B) (−1 + x, y, z; 2.98 Å) and O(51B)···O(32B) ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; 2.61 Å). A longer intermolecular bis(carboxylate)-bridged dimer

Table 1 Atomic coordinates ($\times 10^4$) for complexes **1** and **2**

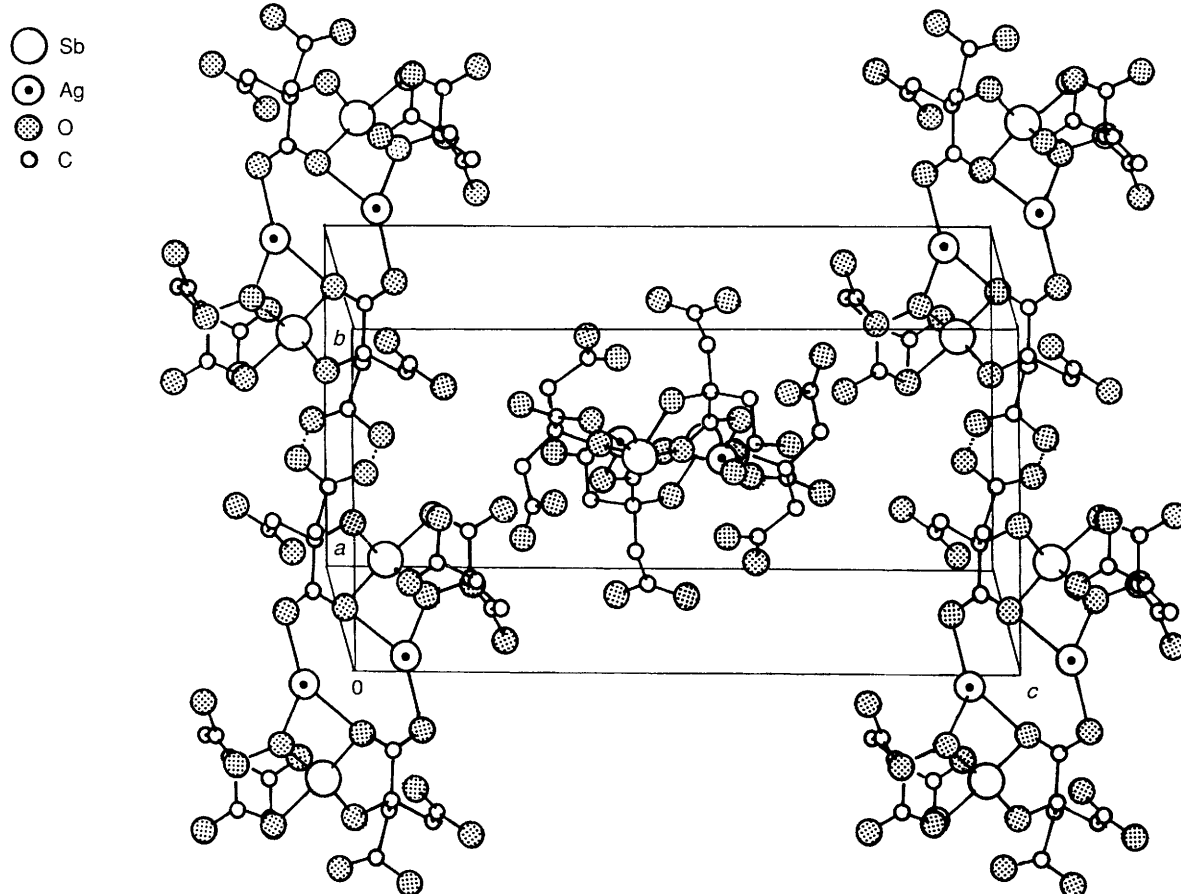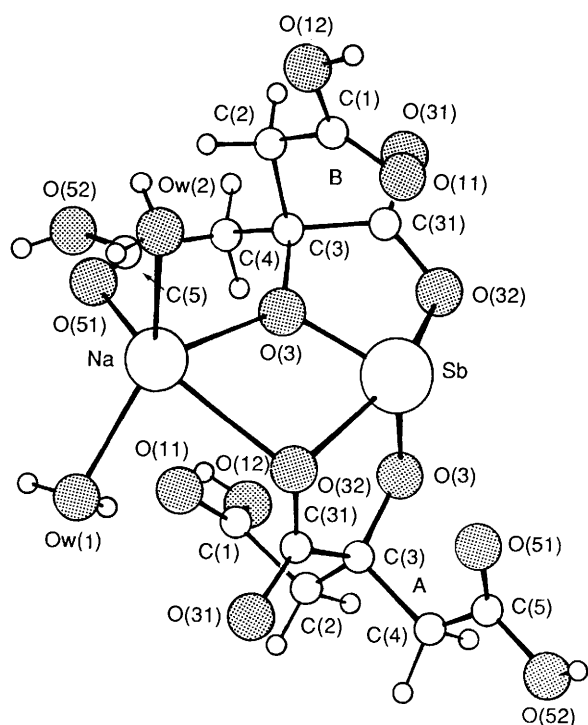| Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Complex 1							
Ag	307(0.5)	336(0.3)	768(0.2)	O(52A)	3 085(5)	5 229(2)	−714(2)
Sb(1)	5 674(0.3)	1 471(0.2)	713(0.1)	C(1B)	905(5)	2 871(3)	1 318(2)
C(1A)	6 568(6)	2 133(3)	−998(2)	O(11B)	−186(4)	2 569(3)	818(1)
O(11A)	6 887(5)	1 342(2)	−645(2)	O(12B)	1 873(4)	3 829(2)	1 363(1)
O(12A)	7 742(4)	2 419(2)	−1 438(1)	C(2B)	1 453(6)	2 179(3)	1 919(2)
C(2A)	4 767(6)	2 904(3)	−1 003(2)	C(3B)	3 508(5)	1 610(2)	1 874(2)
C(3A)	3 534(5)	2 703(2)	−433(2)	O(3B)	3 383(3)	1 139(2)	1 238(1)
O(3A)	4 759(3)	2 822(2)	188(1)	C(31B)	5 253(3)	2 468(3)	1 968(2)
C(31A)	2 558(5)	1 544(2)	−491(3)	O(32B)	6 177(3)	2 645(2)	1 468(1)
O(31A)	1 309(4)	1 292(2)	−979(1)	O(31B)	5 643(4)	2 950(2)	2 496(1)
O(32A)	3 063(4)	888(2)	−11(1)	C(4B)	3 957(6)	689(3)	2 385(2)
C(4A)	1 693(5)	3 522(2)	−471(2)	C(5B)	5 936(6)	109(3)	2 314(2)
C(5A)	2 373(5)	4 665(3)	−253(2)	O(52B)	5 992(5)	−901(3)	2 506(2)
O(51A)	2 285(4)	5 015(2)	295(1)	O(51B)	7 319(5)	525(3)	2 073(2)
Complex 2							
Sb	3 572.2(1)	995.8(3)	2 281.9(1)	O(11B)	3 636(1)	1 617(3)	714(1)
C(1A)	4 760(2)	3 888(3)	4 101(1)	C(2B)	4 757(2)	4 032(3)	894(1)
O(11A)	5 449(1)	3 613(3)	3 785(1)	C(3B)	4 439(2)	4 263(3)	1 658(1)
O(12A)	4 460(1)	5 575(3)	4 238(1)	O(3B)	4 628(1)	2 637(2)	2 058(1)
C(2A)	4 143(2)	2 418(3)	4 393(1)	C(31B)	3 388(1)	4 697(3)	1 654(1)
C(3A)	3 802(2)	979(3)	3 846(1)	O(31B)	3 078(1)	6 053(2)	1 325(1)
O(3A)	3 344(1)	1 907(2)	3 266(1)	O(32B)	2 892(1)	3 598(2)	2 015(1)
C(31A)	4 621(1)	−178(3)	3 573(1)	C(4B)	4 921(2)	5 942(3)	2 022(1)
O(31A)	5 116(1)	−1 044(2)	4 000(1)	C(5B)	5 954(2)	5 789(3)	2 150(1)
O(32A)	4 719(1)	−178(2)	2 894(1)	O(51B)	6 403(1)	4 384(2)	2 169(1)
C(4A)	3 144(2)	−324(3)	4 225(1)	O(52B)	6 321(1)	7 456(2)	2 273(1)
C(5A)	2 746(1)	−1 873(3)	3 768(1)	Ow(1)	6 783(1)	1 025(2)	3 421(1)
O(52A)	2 200(1)	−2 955(3)	4 127(1)	Ow(3)	1 809(2)	1 812(4)	10 183(1)
O(51A)	2 908(1)	−2 096(2)	3 147(1)	Ow(2)	1 279(1)	4 815(3)	949(1)
C(1B)	4 289(2)	2 482(3)	494(1)	Na	1 101(1)	3 912(1)	2 231(1)
O(12B)	4 654(1)	2 136(3)	−122(1)				

Sb
Ag
O
C

Fig. 2 Packing of complex **1** in the unit cell viewed down a

Table 2 Bond distances (Å) and angles (°) about the co-ordination sphere in complexes **1** and **2**

	1			**2**
Ag–O(31A)	2.314(2)		Na–Ow(1)	2.404(2)
Ag–O(32A′)	2.661(2)		Na–Ow(2)	2.512(2)
Ag–O(3B)	2.323(2)		Na–O(32A)	2.562(2)
Ag · · · Ag′	3.221(1)		Na–O(3B)	2.415(2)
Ag · · · Sb	3.323(1)		Na–O(51B)	2.413(2)
			Na · · Sb	3.665(1)

	1	**2**
Sb–O(3A′)	2.008(2)	1.998(1)
Sb–O(32A′)	2.218(2)	2.153(1)
Sb–O(3B)	2.007(2)	1.988(1)
Sb–O(32B)	2.096(2)	2.164(1)

	1		**1**
O(31A)–Ag–O(32A′)	134.1(1)	O(32B)–Sb–O(32A′)	137.5(1)
O(31A)–Ag–O(3B)	132.4(1)	O(3A′)–Sb–O(32A′)	76.0(1)
O(3B)–Ag–O(32A′)	61.3(1)	Sb–O(3B)–C(3B)	117.5(2)
Ag–O(31A)–C(31A)	109.1(1)	Sb–O(32B)–C(31B)	115.7(2)
Ag′–O(32A)–C(31A)	119.8(1)	Sb–O(3A′)–C(3A′)	119.2(2)
O(3B)–Sb–O(32B)	78.1(1)	Sb–O(32A′)–C(31A′)	101.8(2)
O(3B)–Sb–O(3A′)	105.2(1)	Sb–O(32A′)–Ag	103.5(1)
O(32B)–Sb–O(3A′)	81.0(1)	Sb–O(3B)–Ag	122.3(1)

	2		**2**
Ow(1)–Na–Ow(2)	146.0(2)	O(3B)–Sb–O(3A)	99.0(1)
Ow(1)–Na–O(32A)	81.0(2)	O(3B)–Sb–O(32A)	76.3(1)
Ow(1)–Na–O(3B)	117.5(2)	O(3B)–Sb–O(32B)	77.5(1)
Ow(1)–Na–O(51B)	89.7(2)	O(3A)–Sb–O(32A)	77.7(1)
Ow(2)–Na–O(32A)	118.9(2)	O(3A)–Sb–O(32B)	80.8(1)
Ow(2)–Na–O(3B)	96.5(2)	O(32A)–Sb–O(32B)	142.8(1)
Ow(2)–Na–O(51B)	100.5(2)	Sb–O(32A)–Na	101.7(1)
O(32A)–Na–O(3B)	61.8(2)	Sb–O(3B)–Na	112.3(1)
O(32A)–Na–O(51B)	121.2(2)		
O(3B)–Na–O(51B)	72.6(2)		

Primed atoms are related by inversion symmetry.

Fig. 3 Molecular configuration and atom numbering scheme for complex **2**

association between O(51A) and O(52A) $(1 - x, 1 - y, -z$; 3.05 Å) is typical of, although somewhat weaker than, those found in carboxylic acids generally.[16]

Complex **2**, $[SbNa(C_6H_6O_7)_2(H_2O)_2]\cdot H_2O$.—The sodium antimony citrate complex **2** (Fig. 3) is monomeric, in contrast to the dimeric silver complex **1**. However, the four-co-ordination about antimony is identical to that in **1**, with four oxygen donors from two independent citrate(2 −) residues forming five-membered bis(chelate) rings. The same axial bond elongation involving the two carboxyl oxygens is found [Sb–O 2.315(1) and 2.164(1) Å] with shorter bonds to the α-hydroxyl oxygens [Sb–O 1.988(1) and 1.998(1) Å, O–Sb–O ('bite') 76.3(1)°]. The largest difference is in the O–Sb–O (axial) angle [142.8(1)°], an increase of *ca.* 5°.

With this structure, a bonded oxygen from each of the A and B residues forms bridges to the sodium ion [Na–O(32A) 2.562(2), Na–O(3B), 2.415(2) Å; O–Na–O 61.8(2)°] giving an Sb · · · Na separation of 3.665(1) Å. A third citrate oxygen [O(51B)] also forms a six-membered ring with Na[Na–O 2.413(2) Å]. Two waters [Ow(1) and Ow(2)] complete an irregular five-co-ordination about sodium [Na–O 2.404(2) and 2.512(2) Å]. Two other longer contacts are formed with sodium [O(32B), 2.647 (intermolecular): O(52B), 2.633 Å (intramolecular)], adding stability to the complex system. In addition, a number of intermolecular hydrogen-bonding interactions are found, involving the carboxyl oxygens of the citrate residues, the co-ordinated waters and the lattice water [Ow(3)].

The two independent citrate residues (A and B) in both complexes **1** and **2** are conformationally different, although in both the 'terminal' carboxylic acid groups assume the 'rotated' conformation.[11] Torsion angles within the A and B residues respectively are as follows for **1**: O(11)–C(1)–C(2)–C(3), −172, −81; C(1)–C(2)–C(3)–C(4) 180, −167; C(2)–C(3)–C(4)–C(5) −76, +178; C(1)–C(2)–C(3)–C(31) −63, +71; C(3)–C(4)–C(5)–O(51) −98, +25 and C(2)–C(3)–C(31)–O(31) −61, +64°. Comparative angles for **2** are: −54, −171; −177, −177; −179, −66; +65, −61; +179, −20 and −123, −57°.

The structures of complexes **1** and **2** contrast with the distinctive anion–cation interactive associations found for the metal(I)/metal(II)–antimony tartrates yet they show the physical characteristics (*i.e.* stability, crystallinity, diffraction properties) normally associated with ionic compounds. It is therefore assumed that atomic associations involving these univalent species are important in promoting crystal stabilisation with the antimony(III) citrate bis(chelate) system. A similar observation was made for the silver(I) antimony(III) tartrate structure.[1] The main difference in this structure is the occurrence of the stable bis[tartrato(4 −)]antimonate(III) dimer anions, which restrict the number of available oxygens for association with silver. The result is a three-dimensional polymer structure, with additional waters completing the co-ordination about the silver ions. In addition, the versatility of the α-hydroxycarboxylate residue of the citrate ligand as a chelating agent for the stabilisation of water-soluble antimony(III) complexes is recognised.

References

1 Part 1, D. S. Sagatys, G. Smith, D. E. Lynch and C. H. L. Kennard, *J. Chem. Soc., Dalton Trans.,* 1991, 361.
2 C. A. McAuliffe, in *Comprehensive Coordination Chemistry,* ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 3, p. 237.
3 M. C. Poore and D. R. Russell, *Chem. Commun.,* 1971, 18.

4 I. F. Burshtein, G. A. Kiosse, A. B. Ablov, T. I. Malinovskii, B. M. Schedrin and N. V. Rannev, *Dokl. Acad. Nauk SSSR*, 1978, **239**, 90.

5 G. M. Sheldrick, SHELXS 86, Structure Solution Package, University of Göttingen, 1986.

6 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

7 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

8 R. E. Tapscott, R. L. Belford and I. C. Paul, *Coord. Chem. Rev.*, 1969, **4**, 323.

9 M. E. Gress and R. A. Jacobsen, *Inorg. Chim. Acta*, 1974, **8**, 209.

10 I. Zviedre, V. Zavadnik and G. Kolensnikova, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1983, 387.

11 R. Mariezcurrena and S. E. Rasmussen, *Acta Crystallogr., Sect. B*, 1973, **29**, 1035.

12 R. E. Tapscott, *Prog. Inorg. Chem.*, 1982, **8**, 253.

13 F. Charbonnier, R. Faure and H. Loiseleur, *Rev. Chim. Miner.*, 1981, **18**, 245.

14 T. C. W. Mak, W.-H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *Aust. J. Chem.*, 1986, **39**, 541.

15 T. C. W. Mak, W.-H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *J. Chem. Soc., Dalton Trans.*, 1988, 2353.

16 L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 775.