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The Structure of (Hydrogen Ethylenediaminetetraacetato)antimony(III) Dihydrate $Sb(C_{10}H_{13}N_2O_8)\cdot 2H_2O$

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The crystal and molecular structure of the title complex has been determined by X-ray diffraction using 1882 reflections. The crystal was orthorhombic, with the space group $Pbn2_1$; $a=10.98(2)$, $b=18.496(4)$, $c=7.341(9)$, $Z=4$, $D_x=1.99$, $D_m=1.98(2)$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=19.3$ cm^{-1}, and the final R value was 0.036. A distorted ψ-pentagonal bipyramid is formed around the central antimony(III) atom by two nitrogen and two oxygen atoms, together with a lone electron pair at the equatorial positions and two oxygen atoms at the axial positions. One of the Sb–O distances, 2.78 Å, is longer than the others (2.20(2) Å on the average), and it is determined that the carbonyl oxygen is essentially of the free-acid type and that its carbonyl oxygen is weakly coordinated. The splitting of the ν_{as}(COO) band of its infrared and Raman spectra shows the existence of both free and coordinated carboxyl groups. The ^{1}H- and ^{13}C-NMR results show that the antimony(III)–edta complex does not exchange with the free ligand in an aqueous solution at pH 1.5—3.5.

There has been a growing interest in the study of antimony(III) complexes in recent years. Privalova and Ryabenhikov isolated and analyzed 1:1 edta (H_4(edta)=ethylenediaminetetraacetic acid) and other amine-*N*-polycarboxylato complexes of antimony(III).[1] Bhat and Iyer determined the formation constants of the antimony(III)–edta complex,[2] as well as those of the antimony(III)–*N*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetato complex,[3] in an aqueous solution using spectrophotometric and potentiometric methods; the results were reinvestigated by Özer and Bogucki using the potentiometric titration technique.[4] The infrared spectral study was reported by Iyer and Shankar,[5] while the chelatometric titration of antimony(III) using edta was reported by Takamoto[6] and by Yurist.[7]

From these results, it seems that the antimony(III)-edta complex, Sb(Hedta)·n H_2O (n=1,2), should be a very stable compound. Accoding to Bhat,[2] the apparent formation constant of the complex ion [Sb(edta)]$^-$ in an aqueous solution shown by the following equation is about 10^{25}:

$$SbO^+ + 2H^+ + (\text{edta})^{4-} = [Sb(\text{edta})]^- + H_2O$$

In fact, the antimony(III)–edta complex does not decompose even in an acid medium with a pH of 2. However, the antimony in the edta chelate can easily and almost immediately be replaced by zinc, copper, or other metals in an aqueous solution over pH=4, and the back titration with a metal salt solution is possible only under limited conditions.[6,7]

To study this interesting complex, the present authors have determined the crystal and molecular structure of the acid chelate, Sb(Hedta)·2 H_2O, by the X-ray diffraction method: its infrared and Raman spectra were also examined. Moreover, the state of the complex in an aqueous solution was investigated by means of the NMR technique.

Experimental

Syntheses of Chelates. *(Hydrogen Ethylenediaminetetraacetato)antimony(III) Dihydrate*; $Sb(C_{10}H_{13}N_2O_8)\cdot 2H_2O$: This compound was prepared by a slight modification of the method of Bhat;[2] the drop-by-drop addition of antimony(III) chloride in 1 M hydrochloric acid into 0.1 M Na_2H_2(edta) precipitates the complex (1 M=1 mol dm^{-3}). The drop-by-drop addition is essential; if the two solutions are mixed all at once, only H_4(edta) and the hydroxide of antimony(III) are obtained. The complex was partly hydrolized when it was recrystallized from water. The mixed solvent of acetonitrile and water (3:1 v/v) was good for the purpose. The analytical results support the chemical composition: $SbC_{10}H_{17}N_2O_{10}$. Found: Sb, 26.8; C, 27.01; H, 3.78; N, 6.20%. Calcd for $SbC_{10}H_{17}N_2O_{10}$: Sb, 27.23; C, 26.87; H, 3.83; N, 6.27%. Formula weight per 1 mol of edta, Found 453; Calcd, 447.

Sodium Ethylenediaminetetraacetatoantimony(III) Trihydrate: $Na[Sb(C_{10}H_{12}N_2O_8)]\cdot 3H_2O$: This salt was obtained by neutralizing the acid-form complex with a calculated quantity of sodium hydroxide, followed by the evaporation of the water. A more convenient procedure was to mix calculated quantities of Na_4(edta) in an acetic acid–sodium acetate (1:1) buffer, and of antimony(III) chloride. The salt was purified by reprecipitation from water–methanol. Found: Sb, 24.7; C, 24.58; H, 3.76; N, 5.75%. Calcd for $NaSbC_{10}H_{18}N_2O_{11}$: Sb, 25.00; C, 24.66; H, 3.73, N, 5.75%. Formula weight per one mol of edta; Found: 482; Calcd: 487.

X-Ray Measurements. The single crystals of Sb(Hedta)·2 H_2O were obtained as colorless thin plates, which were stable in open air. As they were too brittle, a crystal 0.3×0.1×0.3 mm in size was used for the X-ray measurements without any more reshaping.

Formerly, this crystal was thought to be monoclinic.[8] However, we found that when new axes, a,b, and c, were chosen as follows, the new α,β, and γ were all 90°.

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} \quad \left(\begin{array}{l}\text{Where } a', b', \text{ and } c' \\ \text{are former axes of the} \\ \text{monoclinic unit cell.}^{8)}\end{array}\right)$$

The new space group was confirmed by the results of the reinvestigation of the Weissenberg photographs, as well as the systematic absence of the reflections. Consequently, the results of the present analysis are essentially identical with those of the previous paper,[8] although they are more refined. The crystallographic data are as follows: $SbC_{10}H_{17}N_2O_{10}$, F.W.=447.01, orthorhombic, space group $Pbn2_1$, $Z=4$, $a=10.98(2)$, $b=18.496(4)$, $c=7.341(9)$ Å, $D_x=1.99$, $D_m=1.98(2)$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=19.35$ cm^{-1}.

The reflections within the range of $2\theta<60°$ were collected by Rigaku automated four-circle diffractometer, applying the ω-2θ scan technique. Independent 1882 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for the absorption and extinction. All the calculations were carried out on a HITAC 8700/8800 computer at the Computer Center of The University of Tokyo, using the local version of UNICS.[9] The atomic scattering factors, and the corrections for the anomalous scattering of the antimony atom were taken from authentic tables.[10]

Structure Determination. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. The position of the antimony atom was obtained from the three-dimensional Patterson function, while the positions of all the other non-hydrogen atoms were successively located by Fourier syntheses. The positions of the hydrogen atoms were calculated and fixed. Their isotropic temperature factors were all assumed to be 5.0, which was twice the value of the average isotropic temperature factor of the bonded carbon atoms.

In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R-value was 0.036.[11]

It was difficult to determine the chirality of the crystal from the discrepancy indices. The reversal of the sign of all the z coordinates gave the final R-value of 0.037 after the refinement. Although a slight difference between the final R-values is found between them, it is likely to be within the range of error. Therefore, the former polarity of the crystal was adopted.

The Other Measurements. The infrared spectra of the samples were obtained by means of a JASCO infrared spectrophotometer, type 403G, using Nujol and hexachloro-1,3-butadiene mull.

The Raman spectra of Sb(Hedta)·2 H_2O (crystalline powder packed in a glass capillary tube ($\phi=0.5$ mm) were measured by means of a JEOL LASER Raman spectrophotometer, type JRS-409D, using the JLG-A4 argon-ion LASER.

The proton NMR spectra were obtained by means of a JEOL-JNM-MH-100 (100 MHz) NMR spectrometer, using about a 0.2 mol dm^{-3} D_2O solution of samples at 26 °C with DSS (Sodium 3-(trimethylsilyl)-1-propanesulfonate, $\delta=$ 0 ppm) and *t*-butyl alcohol ($\delta=1.27$ ppm downward from DSS) as the internal standards. The carbon-13 NMR were obtained by means of a JEOL C-60-HL spectrometer (15 MHz for ^{13}C-NMR), using a $\phi=8$ mm sample tube and using acetic acid and cyclohexane as the external standards. The results were obtained from 32- to 128-times accumulation of the measurements.

The pH of the solution was the direct reading of the pH-meter (HM-5A type Toa Denpa Kogyo); the pD values were not corrected, as the composition of the sample solution was not always simple.

Results and Discussion

The final atomic parameters, except those for hydrogen atoms, are listed in Table 1,[12] the interatomic distances, in Table 2, and the bond angles, in Table 3. The perspective drawing of the complex and the numbering scheme of atoms are shown in Fig. 1, and a projection of the structure along the *c*-axis, in Fig. 2.

The Sb, N(1), N(2), O(4), and O(6) atoms are almost on a plane; the deviations of these atoms from the calculated best plane are shown in Table 4. The bond angles, N(1)–Sb–N(2), N(1)–Sb–O(4), and N(2)–Sb–O(6), were in the range of 64—77°; however, that of O(4)–Sb–O(6) was 149.6°, almost twice the former ones. This is due to the existence of a lone electron pair in this direction. The small angles of N–Sb–N and N–Sb–O cannot be explained only by the elongated metal–O and metal–N bond lengths compared with those of the first transition-metal edta complexes.

Therefore, the central metal in this chelate is in a

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B/Å^2), WITH THE ESTIMATED STANDARD DEVIATIONS OF THE NON-HYDROGEN ATOMS

Atom	x	y	z	B_{eq}
Sb	902.0(2)	2382.8(4)	7500	1.9
O(1)	−2361(3)	3274(2)	5469(7)	3.0
O(2)	−991(3)	2513(3)	6626(8)	2.3
O(3)	2635(4)	4702(3)	7034(7)	3.6
O(4)	1717(5)	3770(2)	8353(7)	4.0
O(5)	−766(4)	313(3)	7752(10)	3.6
O(6)	349(4)	1276(2)	8405(7)	3.1
O(7)	4049(4)	1548(4)	5038(10)	4.2
O(8)	2756(4)	2237(3)	6523(7)	2.9
N(1)	947(3)	3213(3)	5021(7)	1.9
N(2)	745(4)	1648(3)	4966(7)	1.9
C(1)	1140(5)	2797(3)	3328(8)	2.1
C(2)	419(5)	2085(3)	3345(7)	2.1
C(3)	−271(4)	3575(3)	5057(8)	2.3
C(4)	−1280(5)	3084(3)	5757(8)	2.1
C(5)	1921(5)	3778(3)	5101(9)	2.6
C(6)	2046(5)	4082(3)	6985(9)	2.6
C(7)	−210(5)	1094(3)	5298(8)	2.5
C(8)	−211(5)	866(3)	7285(9)	2.4
C(9)	1949(5)	1280(3)	4735(8)	2.5
C(10)	3012(5)	1724(3)	5463(9)	2.6
O(W1)	2700(4)	5249(3)	10221(8)	3.4
O(W2)	5328(7)	304(4)	6502(11)	5.9

TABLE 2. INTERATOMIC DISTANCES (l/Å), WITH THE ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Sb-N(1)	2.382(5)	C(3)-N(1)	1.495(7)
Sb-N(2)	2.311(5)	C(5)-C(6)	1.499(9)
Sb-O(2)	2.188(5)	C(5)-N(1)	1.497(7)
Sb-O(4)	2.788(5)	C(7)-C(8)	1.519(9)
Sb-O(6)	2.236(5)	C(7)-N(2)	1.485(7)
Sb-O(8)	2.175(5)	C(9)-C(10)	1.524(8)
O(1)-C(4)	1.256(7)	C(9)-N(2)	1.497(7)
O(2)-C(4)	1.273(8)	N(1)-C(1)	1.477(8)
O(3)-C(6)	1.316(8)	C(1)-C(2)	1.538(8)
O(4)-C(6)	1.214(8)	C(2)-N(2)	1.482(7)
O(5)-C(8)	1.238(8)	O(W1)···O(3)	2.550(8)
O(6)-C(8)	1.227(7)	O(W2)···O(7)	2.902(10)
O(7)-C(10)	1.225(7)	O(W1)···O(5)^{I}	2.714(8)
O(8)-C(10)	1.259(8)	O(W1)···O(1)^{II}	2.764(6)
C(3)-C(4)	1.522(8)	O(W1)···O(W2)^{III}	2.952(10)

Key to symmetry operations: I. $0.5+x$, $0.5-y$, $0.5+z$; II. $-x$, $1.0-y$, $0.5+z$; III. $-0.5+x$, $0.5-y$, $0.5+z$.

TABLE 3. BOND ANGLES (ϕ/°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

N(1)-Sb-N(2)	76.5(2)	C(7)-N(2)-C(9)	109.2(4)
N(1)-Sb-O(2)	74.0(2)	Sb-O(2)-C(4)	118.4(3)
N(1)-Sb-O(4)	64.7(2)	Sb-O(4)-C(6)	110.4(4)
N(1)-Sb-O(8)	79.0(2)	Sb-O(6)-C(8)	119.0(4)
N(2)-Sb-O(2)	76.0(2)	Sb-O(8)-C(10)	120.4(4)
N(2)-Sb-O(6)	71.4(2)	O(2)-C(4)-O(1)	123.5(5)
N(2)-Sb-O(8)	74.4(2)	O(2)-C(4)-C(3)	118.8(5)
O(2)-Sb-O(4)	105.6(1)	O(1)-C(4)-C(3)	117.7(5)
O(2)-Sb-O(6)	86.0(2)	O(4)-C(6)-O(3)	122.6(6)
O(2)-Sb-O(8)	143.7(2)	O(4)-C(6)-C(5)	123.9(5)
O(4)-Sb-O(6)	149.6(2)	O(3)-C(6)-C(5)	113.4(5)
O(4)-Sb-O(8)	83.5(1)	O(6)-C(8)-O(5)	123.4(6)
O(6)-Sb-O(8)	103.8(2)	O(6)-C(8)-C(7)	116.9(5)
Sb-N(1)-C(1)	108.1(3)	O(5)-C(8)-C(7)	119.8(6)
Sb-N(1)-C(3)	104.9(3)	O(8)-C(10)-O(7)	124.5(6)
Sb-N(1)-C(5)	115.8(3)	O(8)-C(10)-C(9)	116.9(5)
C(1)-N(1)-C(3)	112.1(4)	O(7)-C(10)-C(9)	118.6(5)
C(1)-N(1)-C(5)	107.1(4)	N(1)-C(3)-C(4)	113.0(4)
C(3)-N(1)-C(5)	109.0(4)	N(1)-C(5)-C(6)	111.3(5)
Sb-N(2)-C(2)	110.1(3)	N(2)-C(7)-C(8)	110.5(5)
Sb-N(2)-C(7)	109.0(3)	N(2)-C(9)-C(10)	113.0(4)
Sb-N(2)-C(9)	107.0(3)	N(1)-C(1)-C(2)	111.5(5)
C(2)-N(2)-C(7)	109.7(4)	N(2)-C(2)-C(1)	110.5(4)
C(2)-N(2)-C(9)	111.7(4)		
O(W1)···O(3)-C(6)	112.6(4)		
O(W2)···O(7)-C(10)	124.5(5)		
O(3)···O(W1)···O(5)^{I}	119.6(3)		
O(3)···O(W1)···O(1)^{II}	116.7(3)		
O(3)···O(W1)···O(W2)^{III}	97.5(2)		
O(5)^{I}···O(W1)···O(1)^{II}	114.6(3)		
O(5)^{I}···O(W1)···O(W2)^{III}	101.4(3)		
O(1)^{II}···O(W1)···O(W2)^{III}	101.7(2)		
O(7)···O(W2)···O(W1)^{IV}	125.7(3)		

Key to symmetry operations: I. $0.5+x$, $0.5-y$, $0.5+z$; II. $-x$, $1.0-y$, $0.5+z$; III. $-0.5+x$, $0.5-y$, $0.5+z$; IV. $0.5+x$, $0.5-y$, $-0.5+z$.

TABLE 4. LEAST-SQUARES PLANES AND THE DEVIATIONS OF ATOMS (l/Å)

Plane(1) [Sb, N(1), N(2), O(4), O(6)]
$0.95973X-0.26305Y-0.098592Z+0.71985=0$
Sb −0.032, N(1) −0.209, N(2) +0.344, O(4) +0.090, O(6) −0.142

Plane(2) [C(3), C(4), O(1), O(2)]
$0.01008X-0.50894Y-0.86074Z+6.56170=0$
C(3) −0.002, C(4) +0.007, O(1) −0.002, O(2) −0.002

Plane(3) [C(5), C(6), O(3), O(4)]
$0.87836X-0.47137Y+0.07936Z+1.15408=0$
C(5) +0.010, C(6) −0.025, O(3) +0.006, O(4) +0.010

Plane(4) [C(7), C(8), O(5), O(6)]
$0.83334X-0.53324Y-0.14557Z+1.83477=0$
C(7) −0.003, C(8) +0.009, O(5) +0.003, O(6) −0.003

Plane(5) [C(9), C(10), O(7), O(8)]
$-0.05604X+0.61186Y-0.78898Z+1.41084=0$
C(9) −0.003, C(10) +0.013, O(7) −0.005, O(8) −0.005

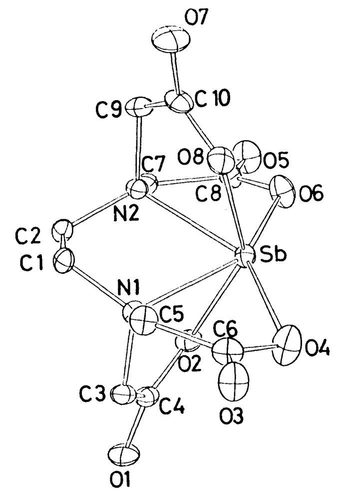

Fig. 1. The perspective drawing of Sb(Hedta)·$2H_2O$ and the numbering scheme of non-hydrogen atoms.

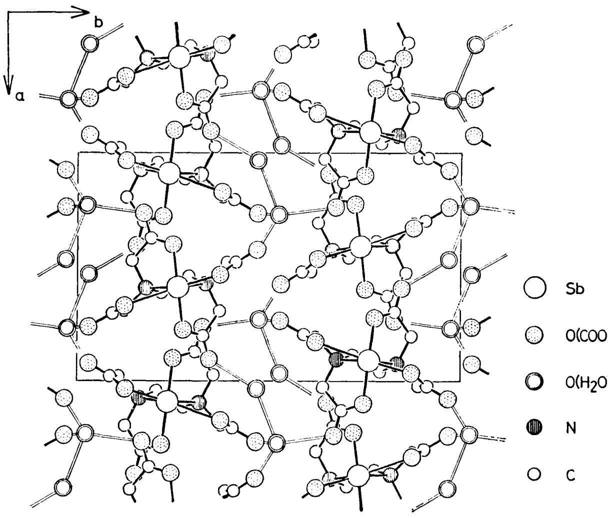

Fig. 2. The projection of the structure along the c axis.
(=: Hydrogen bonding)

ψ-pentagonal bipyramidal environment. The hepta-coordinated pentagonal bipyramidal structure is found in several edta chelates such as $\mathrm{Rb[Fe^{III}(edta)(H_2O)]\cdot H_2O}$,13) $\mathrm{Sn[Sn^{II}(edta)(H_2O)]\cdot H_2O}$,14) and $\mathrm{[Mg(H_2O)_6][Mg(edta)(H_2O)]\cdot 2H_2O}$.15)

Moreover, such hexa-coordinated metal chelates, *i.e.*, ψ-hepta-coordinated ones including a lone pair, are also found in the complexes of bivalent group IVB metals or of tervalent group VB metals.14,17,18) In the cases of tris(oxalato)antimonate(III),15) and of tris(diphenylthiophosphinato)antimony(III),16) the lone pair is in the axial direction, which is more desirable from the point of view of VSEPR consideration19) than the structure of this antimony(III)–edta complex. As the coordinating atoms of an edta cannot occupy all of the five positions of a planar pentagon because of its steric hindrance, the lone-pair electrons seem to occupy the equatorial direction. The O(2)–Sb–O(8) axis bends in the direction opposite to the lone pair, because the repulsion from the lone-pair electrons is stronger than the other bonding-pair ones. The Sb–

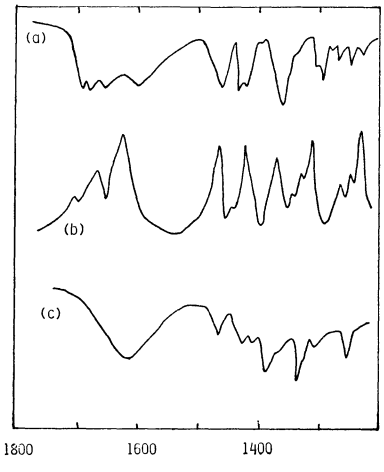

Fig. 3. Infrared (a), and Raman (b) spectra of (hydrogen ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)antimony(III) dihydrate, and infrared spectra of its sodium salt (c).

O(2) and Sb–O(8) bonds make angles of 65.7, and 74.4° respectively with respect to the average Sb–N(1)–N(2)–O(4)–O(6) plane.

Antimony(III), generally, does not make a strong bond with a nitrogen atom of amines. As antimony(III) has a strong affinity to a hydroxo group, when some amine is added, it reacts with the hydroxo group produced by the hydrolysis of an amine, except under a strictly dry medium. The Sb–N distances of this complex are shorter than that of the $SbCl_3$–aniline adduct (2.525 Å),[20)] and the Sb–N bond of this edta complex is stronger than that of the common antimony(III)–amine complexes.

With respect to the bond lengths of Sb–O and of C–O, there are two types of carboxyl groups in the chelate: Type 1: the bond lengths of Sb–O(2), Sb–O(6), and Sb–O(8) are in the range of 2.18 and 2.24 and are normal.[17,21–26)] The difference between the two C–O bond lengths of each carboxyl group of this type is in the range of 0.02 and 0.04 Å, like the usual ionized carboxyl group.[27a)] Type 2: Sb–O(4) distance, 2.79 Å, is out of the ordinary. The C(6)–O(3) is longer than C(6)–O(4) by 0.10 Å, which is comparable with the value of a free carboxylic acid. Therefore, this type of carboxyl group is likely to be in a free-acid form, coordinating to an antimony atom with its carbonyl oxygen atom. This type of coordination seems to cause the especially strong acidity of Sb(Hedta) ($pK_a=1.02$).[4)] Of all the carboxyl groups, the Type 2 group has the largest deviations from the best plane, as is shown in Table 4. This phenomenon is also found at the coordinated-acid-form carboxyl group in $[Cu(H_2edta)(H_2O)]$.[28)]

One of the crystalline water oxygen atoms, O(W1), forms a hydrogen bond with O(3) of the Type 2 carboxyl group. This O(3)–H⋯O(W1) distance is 2.55 Å, and it agrees with that of a hydrogen bond between a water and an acid.[27b)] The other hydrogen bonds of the crystalline-water oxygens are those between O(W1)⋯O(5)$^{\mathrm{I}}$, O(W1)⋯O(1)$^{\mathrm{II}}$, O(W1)⋯O(W2)$^{\mathrm{III}}$, and O(W2)⋯O(7), as is shown in Table 2 and Fig. 2, where O(1), O(5), and O(7) are all Type 1 carboxyl-group oxygen atoms.

The infrared and Raman spectra of the complex have essentially the same absorption bands; almost all peaks of the infrared spectra were recognized also in its Raman spectra between 200 and 4000 cm^{-1}. The spectra between 1200 and 1800 cm^{-1} are shown in Fig. 3. In the case of Sb(Hedta)·2 H_2O, the ν_{as}(COO) peak in the infrared spectra splits into 4 peaks, and that in the Raman spectra, into 3 peaks.

The band at 1693 cm^{-1} of the infrared spectra (1702 cm^{-1} in Raman spectra) shows the existence of a free carboxyl group, while the 1677 and 1651 cm^{-1} bands of the infrared spectra (1667 cm^{-1} band of the Raman spectra) are those of the coordinated carboxyl groups; both of them are ν_{as}(COO) bands. Although some additional splitting is recognized in the spectra of this region, it is probably due to the difference in the effects on each carboxyl group of its coordination bond, its position in the ψ-pentagonal bipyramidal configuration, and the hydrogen bonds of crystalline waters around it.

According to Nakamoto[29b,c)] and Sawyer,[30–32)] the ν_{as}(COO) band of metal-edta chelates appears at about 1650 cm^{-1}, when the coordinate bond is a rather covalent-dominant one. As has been shown above, the wave numbers of the band of the Sb–edta complex are higher than those of typical covalent-dominant edta complexes, such as Cr(III) (1640 cm^{-1}), Co(III) (1645 cm^{-1}), and Th(IV) (1630 cm^{-1}).[32)]

The sodium salt of the antimony(III)–edta complex has a broad ν_{as}(COO) band at about 1630 cm^{-1}, lower than that of the free-acid-type complex. This effect is due to the more ionic character of the Type 2 carboxyl group in this salt.

Like the edta complexes of other metals,[29c,30–32)] four bands in the 1302—1470 cm^{-1} region, which are likely ν_s(COO) or its mixing bands, were observed in the infrared as well as in the Raman spectra.

In the far-infrared region, the band near 240 cm^{-1} is tentatively assigned as the ν(Sb–O) band, and those in the 370—390 cm^{-1} region, as the ν(Sb–N) modes, by analogy to the amino-acid complexes of several metals.[29a)]

This antimony(III)–edta complex can also exist even in an aqueous solution of a limited pH region, in spite of the tendency of the common antimony(III) salt to be easily hydrolyzed, a fact which is proved by the NMR spectral data to be shown below.

In the cases of covalent-dominant edta complexes, such as Co(III)–,[33)] Zr(IV)–,[34)] and Hf(IV)–edta,[34)] the AB pattern was observed in their ^1H-NMR spectra due to the fixation of the ligand. In the case of the Bi(III)–edta complex, as well as of the Sb(III)-*trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid complex, both of them can be expected to have a structure very near to that of the antimony(III)–edta complex, and the acetato-proton peak splits into an AB-pattern quartet due to the spin-spin coupling of geminal protons, as the nitrogen atoms of the ligand in these complexes bond tightly with the central metal. The typical ^1H-NMR spectra of Sb(Hedta)·$2H_2O$ in an aqueous solution containing a sodium acetate–

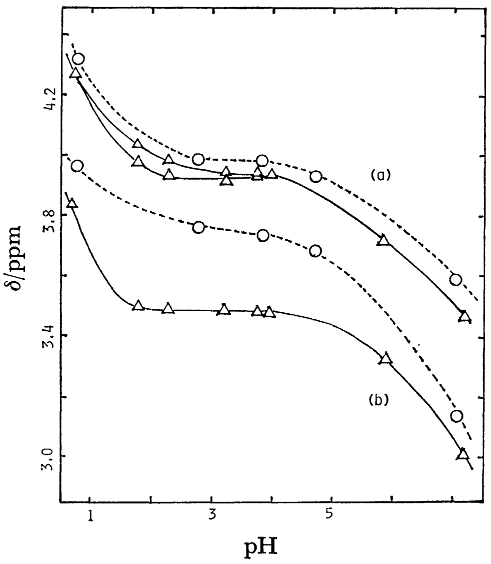

Fig. 4. Chemical shifts of acetato (a), and ethylene (b) protons of Sb(Hedta) complex (--○--) compared with those of sodium salt of edta (—△—) in D_2O solution. (δ: DSS = 0, downwarp +) (pH shown is the reading of a pH meter; correction for D_2O was not applied).

acetic acid buffer show two peaks; one for the acetato-protons, and the other for ethylene-protons of the ligand. The acetato-proton peak clearly splits into two or more peaks in the pH region of 1.5—3.5, with a splitting of 3 Hz. The ethylene-proton peak also seems to have some fine structure when the pH of the solution is in the same region. However, the splitting is too small to be identified clearly.

The relations between the pH of the solution and the chemical shifts of acetato- and ethylene-protons of the ligand in the antimony(III)–edta complex are shown in Fig. 4. As is shown in the figure, when the pH of the solution was between 1.5—3.5, the chemical shifts of both peaks, especially those of the ethylene-protons, are different from those of the sodium salt of edta. This fact seems to show that the edta ligand in the antimony(III)–edta complex bonds with the metal atom only in the 1.5—3.5 pH region. This fact coincides with the result of a potentiometric titration study by Özer.[4]

When disodium salt of edta is added to the solution of the antimony(III)–edta complex in the pH region of 1.5—3.5, a new peak due to the ethylene-proton of the $[H_2(edta)]^{2-}$ ion appears, in addition to the original two peaks of the antimony complex (The acetato-proton peak of the excess salt could not be recognized; it is probably due to the accidental overlapping of the peaks of the antimony complex with that of the disodium salt.) From this fact, it can be said that the edta ligand in the antimony complex does not exchange with the free ligand ion in the aqueous solution of this pH region; this is a proof of the strong covalent character bond between the ligand and the central metal atom of the complex.

Although the ^{13}C-NMR of the acid-type complex Sb(Hedta) could not be measured by our spectrometer because of its low solubility, its sodium salt was examined by the technique. The peak for its carboxyl carbons, 176.6; for ethylene carbons, 62.0: for acetato-methylene carbons, 57.0 (δ ppm, downward from TMS). No splitting of the carboxyl carbon peak was found. The ethylene and acetato methylene carbon peaks of the antimony complex shift to a lower magnetic field than the tetra- and disodium salts of the free ligand. (Na_4(edta): 181.0, 60.4, and 53.5; Na_2H_2(edta): 171.5, 58.9, and 52.5 ppm, respectively, for carboxyl, ethylene, and acetato-methylene carbons.) As the chemical shifts of both types of ligand carbons are very different from those of the free ligand, it is likely that the edta ligand in this complex does not dissociate from the central antimony(III) atom, not even in the aqueous solution. The chemical shifts of the carboxyl carbons in some metal-edta complexes were shown by Hagen and others.[35] Compared with their data, the resonances of the carbon atoms of the antimony(III)–edta chelate appear in a relatively higher magnetic field than the corresponding peaks of common edta complexes.

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