研究简报

三氯化锑和二氧杂环己烷配合物[$SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}$]的合成与晶体结构

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Synthesis and Crystal Structure of the Complex of Antimony Trichloride and Dioxane

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New solid complex of the antimony trichloride and dioxane was obtained through a reaction of the dioxane and the absolute methanol solution of the antimony trichloride. The formula of the complex is [$SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}$]. The crystal structure of the complex belongs to cubic system, space group I-43d, $a = 17.1417(5)$ Å, $Z = 16$. The trivalent antimony ion not only bonds directly to three chlorine anions, but also is coordinated by three oxygen atoms of the dioxane molecules. Two oxygen atoms in a dioxane molecule will coordinate to different antimony ions, respectively.

Keywords: dioxane complex of antimony trichloride synthesis crystal structure

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The formation of many complexes occur in the solution, to study the interaction between the solute and solvent molecule is interesting not only for the solution chemistry, but also for the coordination chemistry of the elements. Because the inorganic salts of some main group elements, such as antimony trichloride, are hydrolyzed very easily in the aqueous solution, the synthesis of the many complexes for such elements must conduct in the non-aqueous solution. Some non-aqueous solvents, for example, acetonitrile and dimethyl sulfoxide, are donor ligand. The adducts or complexes of the antimony and bismuth and some donor solvents were reported[1~5]. Dioxane $(CH_2)_4O_2$ is a non-aqueous solvent. The oxygen atoms in the dioxane possess the lone electron pair, hence, the dioxane also is a donor solvent. To understand whether the complex formation between $SbCl_3$ and $(CH_2)_4O_2$ can occur and which coordination structure the complex will possess is useful for the antimony chemistry. Here, we shall report the synthesis process and the single-crystal structure.

1 Experimental

1.1 Synthesis

All the chemicals used in the experiments are analytical reagent. The antimony content is determined by the iodometry and the chlorine is measured by the ion selective electrode. The preparation of the single-crystal of the complex of antimony trichloride and dioxane: to dissolve 6.9g (about 28.5mmol) antimony trichloride in 10ml absolute methanol. Then, to add 10.0mL dioxane to the methanol solution of the antimony trichloride, the dioxane being kept in excess of the stoichiometric amount. The above solution is stirred and the reaction conducts at room temperature for 5h. The white solid complex is collected by filtration. The resultant is dried in the vacuum drying oven at 40℃. At last, the recrystallization from the absolute methanol solution of the resultant will give the needle crystal. The crystal is moisture in air. The analysis results show that the formula of the resultant is $[SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}]$ (Found: Sb, 34.15% and Cl, 29.81%. Theory: Sb, 33.79% and Cl, 29.52).

1.2 Crystal Structure

The crystal data are acquired on a single-crystal specimen(0.60×0.50×0.35mm) by Rigaku RAXIS RAPID Imaging Plate diffractometer at 173K. The data after the absorption correction are used in the full-matrix least-squares refinement. The crystal data and some results are summarized in Table 1. The selected bond lengths and bond angles in the complex are listed in Table 2.

2 Results and Discussion

As Fig. 1 shows, each antimony ion not only bonds directly to three chlorine anions, but also is coordinated by three oxygen atoms from three dioxane molecules. From Table 2, we find that the length of three Sb-Cl bonds and the angle of three Cl-Sb-Cl bonds are the same. Therefore, the antimony ion and three chlorine anions form a trigonal pyramidal polyhedron. The covalent radius of the antimony and chlorine atom is 1.40Å and 0.99Å, respectively. The sum(2.39Å) of the covalent radii of the antimony and chlorine atom is slightly larger than the length(2.3784Å) of the Sb-Cl bond in the complex. The shortest length of the Sb-Cl bond and the angle of the Cl-Sb-Cl bond in

Table 1　Crystal Data and Structure Refinement for the Complex of Antimony Trichloride and Dioxane

empirical formula	$C_6H_{12}O_3Cl_3Sb$
formula weight	306. 26
crystal system	cubic
space group	I-43d
cell constants	
a/Å	17. 1417(5)
V/Å^3	5037. 1(10)
Z	16
$D_{cal.}$/(g · cm^{-3})	1. 900
crystal size	0. 60 × 0. 50 × 0. 35mm
temperature	173(2)K
radiation(λ)(Mo $K\alpha$)	0. 71073Å
absorption coefficient	2. 804mm^{-1}
F(000)	2784
theta range for data collection	2. 91° to 27. 44°
index ranges	$1 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 12$
reflections collected/unique	23860/533[R(int) = 0. 0110]
completeness to 2θ = 27. 44°	53. 5%
absorption correction	ABBCOR by higashi
max. and min. transmission	1. 4137 and 0. 6508
refinement method	full-matrix least-square on F^2
data/restraints/parameters	533/0/41
goodness-of-fit on F^2	0. 337
final R indices [$I > 2\sigma(I)$]	R_1 = 0. 0237 wR_2 = 0. 0583
R indices (all data)	R_1 = 0. 0351 wR_2 = 0. 0623
absolute structure parameter	0. 20(12)
extinction coefficient	0. 00385(12)
largest diffraction peak and hole	0. 296 and −0. 285e · Å^{-3}

Table 2　Selected Bond Lengths(Å) and Bond Angle(°) in the Complex of Antimony Trichloride and Dioxane

Sb-Cl(1)#1	2. 3784(17)	O(1)-C(1)	1. 375(9)	Sb-Cl(1)	2. 3784(17)
O(1)-C(2)	1. 336(9)	Sb-Cl(1)#2	2. 3784(17)	C(1)-C(2)#3	1. 350(9)
Sb-O(1)	2. 780(10)	C(2)-C(1)#3	1. 350(9)		

Cl(1)#1-Sb-Cl(1)	93. 19(9)	Cl(1)#1-Sb-Cl(1)#2	93. 19(9)	Cl(1)-Sb-Cl(1)#2	93. 19(9)
C(2)-O(1)-C(1)	115. 4(5)	C(2)#3-C(1)-O(1)	121. 6(8)	O(1)-C(2)-C(1)#3	123. 0(8)

Symmetry transformations used to generate equivalent atoms: #1: z, x, y; #2: y, z, x; #3: $-x+2, -y+3/2, z+0$.

the $SbCl_3$ crystal is 2. 36Å and 95°[6]. Obviously, the length(2. 3784Å) of the Sb-Cl bond in [$SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}$]is slightly larger than that(2. 36Å) of the Sb-Cl bond in $SbCl_3$ and the angle (93. 19°) of the Cl-Sb-Cl bond in [$SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}$] is slightly less than that(95°) of the Cl-Sb-Cl bond in $SbCl_3$. This can be attributed to the coordination of the oxygen atoms in the dioxane to the antimony ion. The trivalent antimony ion possesses three empty 5p orbitals and the oxygen atom in the dioxane possesses the lone electron pair. Therefore, there may be the coordination bonds between an antimony ion and three oxygen atoms from different dioxane molecules through the interaction between the empty 5p orbitals of the antimony ion and the lone electron pair of the oxygen atom. As Fig. 2 shows, two oxygen atoms in one dioxane molecule will coordinate to two antimony

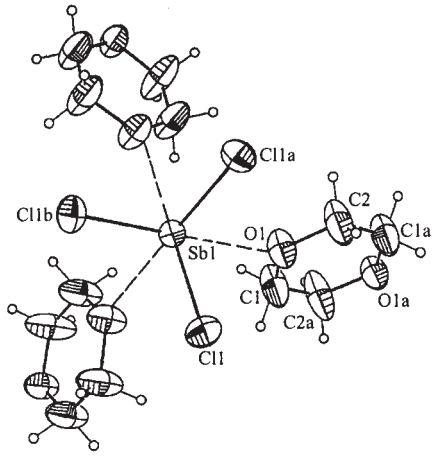

Fig. 1 Molecular structure of $[SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}]$

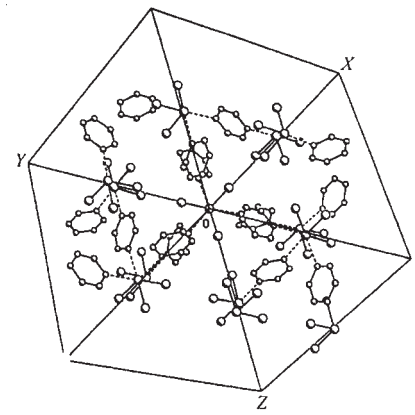

Fig. 2 Projection of $[SbCl_3 \cdot \{(CH_2)_4O_2\}_{1.5}]$

ions, respectively. Perhaps, this is why the molar ratio of the antimony trichloride to the dioxane in the complex is 1∶1.5. The formation of the network structure in the lattice of the complex may also be just because of the presence of the coordination bonds between the antimony ions from two antimony trichloride molecules and two oxygen atoms in same dioxane molecule. The distance between the antimony ion and three oxygen atoms are same. As Fig. 1 and 2 show, the antimony atom and three oxygen atoms can also form a trigonal pyramidal polyhedron. In this case, the coordination number of the antimony ion in the complex is six. However, the distance(2.78Å) between the antimony ion and the oxygen atom in the complex is much larger than the sum(2.13Å) of the covalent radius (1.40Å) of the antimony atom and that(0.73Å) of the oxygen atom. This can be attributable to the steric hindrance caused by the larger molecule volume of the dioxane. So, the coordination bond between the antimony ion and the oxygen atom in the complex must be very weak. This is just why the complex is moisture in air. More detailed research on the complex of the antimony trichloride and dioxane will be suggested to publish elsewhere.

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