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Syntheses and Characterization of One-Dimensional Antimony(III) Diphosphonates: $[NH_3(CH_2)_nNH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ (n=4, 5)

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This paper describes the hydrothermal syntheses and characterization of two antimony(III) diphosphonates: $[NH_3(CH_2)_nNH_3]Sb\{CH_3C(O)(PO_3)_2\}$ [$n = 4$ (1), 5 (2)]. The two compounds are isostructural based on their XRD measurements. Single-crystal structure determination of compound 1 revealed a one-dimensional linear chain structure where the distorted $\{SbO_5E\}$ octahedra (E is the lone pair electrons occupying an axial position) are corner-shared by $\{CPO_3\}$ tetrahedra. The protonated diamines are located between the chains, with their nitrogen atoms locked by the hydrogen bonds with the phosphonate oxygens. Crystal data for 1: orthorhombic, space group Pnma, $a = 13.426(4)$, $b = 17.149(4)$, $c = 5.4496(14)$ Å, $V = 1254.7(6)$ Å^3, $Z = 4$. © 2002 Elsevier Science (USA)

Key Words: **antimony(III); phosphonate; 1-hydroxyethylidenediphosphonate; crystal structure.**

INTRODUCTION

The phosphonate chemistry has been of increasing interest due to their potential applications in ion exchange, catalysis and sensors (1–4). Great efforts have been made in searching for materials with new structure types (5–9). Among these, attention has been paid to the antimony(III) or tin(II) compounds because the stereochemically active lone pairs of electrons associated with each metal center may pose additional influences on the structures of these materials (10–17). So far, examples of antimony(III) phosphonates are still rare, including $Sb_2O(O_3PCH_2PO_3)$, $Sb[O_3P(CH_2)_nPO_2(OH)]$ ($n = 2,3$) (11), $Sb_2O(CH_3PO_3)_2$, $NH_4(Sb_2O)_3(CH_3PO_3)_2$ (12) and $Cl_3SbO(OH)[(C_6H_5CH_2)RPO_2]SbCl_3 \cdot H_2O$ (10). In this paper, we report the syntheses and characterization of two new Sb(III) diphosphonate compounds, namely $[NH_3(CH_2)_4NH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ (**1**) and $[NH_3(CH_2)_5NH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ (**2**).

EXPERIMENTAL

Materials and Methods

The 50% aqueous solution of 1-hydroxyethylidenediphosphonic acid (hedpH_4) was bought from Nanjing Shuguang Chemical factory. All the other starting materials were of reagent grade quality and were obtained from commercial sources without further purification. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a Nicolet IFS66v spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen in the temperature range 30–600°C with a heating rate of 5°C/min on a TGA-DTA V1.1b Inst 2100 instrument.

Synthesis of $[NH_3(CH_2)_4NH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ (1)

In a typical synthesis, a mixture of $SbCl_3$ (0.3424 g, 1.5 mmol), 50% aqueous solution of hedpH_4 (1.3 cm^3, 3.3 mmol) and NaF (0.0426 g, 1 mmol) in 8 cm^3 H_2O, adjusted by 1,4-diaminobutane to pH = 2.9, was kept in a Teflon-lined autoclave at 140°C for 2 d. After slow cooling to room temperature, the colorless needle-like crystals of **1** were collected as a monophasic material, judged by the powder X-ray diffraction pattern. Yield: 0.3016 g (48.7%, based on Sb). Found (calcd.) for $C_6H_{17}N_2O_7P_2Sb$: C, 17.94 (17.45); H, 4.68 (4.15); N, 6.75 (6.79)%. IR (KBr, cm^{-1}): 3444w, 3056-2437(br), 2062w, 1661 m, 1613s, 1560s, 1471 m, 1455 m, 1442 m, 1378 m, 1364 s, 1290w, 1261 m, 1108 s, 1058 s, 1007 s, 889 s, 810 s, 754 s, 671 s, 618 s, 587 s, 550 m. X-ray fluorescence spectrum proved that fluorine was not incorporated into the structure.

Synthesis of $[NH_3(CH_2)_5NH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ (2)

A mixture of $SbCl_3$ (0.3023 g, 1.3 mmol), 50% hedpH_4 (1.0 cm^3, 2.5 mmol) and 8 cm^3 H_2O, adjusted by 1,5-

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diaminopentane to pH = 3.5, was kept in a Teflon-lined autoclave at 140°C for 2 d. After slow cooling to room temperature, the colorless needle-like crystals of **2** were collected as a monophasic material, judged by the powder X-ray diffraction pattern. Yield: 0.1149 g (17.5%, based on Sb). Found (calcd.) for $C_7H_{19}N_2O_7P_2Sb$: C, 20.62 (19.78); H, 4.81 (4.51); N, 6.78 (6.59)%. IR (KBr, cm^{-1}): 3431w, 2964-2642(br), 2113w, 1609s, 1550s, 1469 m, 1442 m, 1378w, 1358 m, 1311w, 1189w, 1106 s, 1069 s, 1014 s, 886 s, 806 s, 732 s, 669 s, 618 s, 586 s, 547 m.

Crystallographic Studies

A single crystal of dimensions 0.8 × 0.04 × 0.04 mm for **1** was selected for indexing and intensity data collection at 298 K on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo*Kα* ($\lambda = 0.71073$ Å) radiation. A hemisphere of data was collected in the θ range 3.259–27.926° using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. Number of measured and observed reflections [$I > 2\sigma(I)$] are 7541 and 1449 ($R_{int} = 0.0620$), respectively. The data were integrated using the Siemens SAINT program (18), with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption and extinction corrections were applied.

The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL (19). All the non-hydrogen atoms in compound **1** were refined anisotropically. All the hydrogen atoms were located from the Fourier maps, and were refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. In the final Fourier-difference map, the deepest hole was -0.554 e$Å^{-3}$, the highest peak 2.339 e$Å^{-3}$ located near Sb1 (0.8330 Å). Crystallographic and refinement details are listed in Table 1. The atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, respectively.

TABLE 1
Crystallographic Data for 1

Formula	$C_6H_{17}N_2O_7P_2Sb$
M	825.81
T (K)	293(2)
Crystal system	Orthorhombic
Space group	*Pnma*
a (Å)	13.426(4)
b (Å)	17.149(4)
c (Å)	5.4496(14)
v ($Å^3$)	1254.7(6)
z	4
D_c (g/cm^{-3})	2.186
F(000)	816
Goodness-of-fit on F^2	1.182
$R1, wR2^a$ [$I > 2\sigma(I)$]	0.0316, 0.0809
(All data)	0.0330, 0.0818
Extinction coefficient (mm^{-1})	0.0016(4)
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e $Å^{-3}$)	2.339, −0.554

$^aR_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1

Atom	*x*	*y*	*z*	U_{eq}
Sb(1)	0.8847(1)	0.7500	−0.8651(1)	0.018(1)
P(1)	0.8006(1)	0.6606(1)	−0.3337(2)	0.018(1)
O(1)	0.8924(2)	0.6624(2)	−0.1655(5)	0.027(1)
O(2)	0.7359(2)	0.5900(1)	−0.2919(5)	0.028(1)
O(3)	0.8267(2)	0.6639(1)	−0.6087(4)	0.028(1)
O(4)	0.7423(2)	0.7500	0.240(6)	0.022(1)
N(1)	0.6716(2)	0.5610(2)	0.1711(6)	0.026(1)
C(1)	0.7349(3)	0.7500	−0.2413(9)	0.018(1)
C(2)	0.6267(4)	0.7500	−0.3191(12)	0.030(1)
C(11)	0.5637(3)	0.5755(2)	0.2173(8)	0.031(1)
C(12)	0.4987(3)	0.5079(2)	0.1368(7)	0.027(1)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized, U_{ij} tensor.

RESULTS AND DISCUSSION

Structural Description

The structure of compound **1** is composed of anionic linear chains of $[Sb\{CH_3C(O)(PO_3)_2\}]_n^{2n-}$ and $[NH_3(CH_2)_4NH_3]^{2+}$ counterions. Figure 1 shows a fragment of the chain with atomic labeling scheme. The Sb atom, sitting in a mirror plane, has a distorted octahedral environment. The four equatorial positions of each $\{SbO_5\}$ octahedron are filled with phosphonate oxygens from two equivalent hedp ligands. The two axial sites are provided by the oxygen, O(4A), and the lone pair electrons of Sb, respectively. The Sb–O bond lengths are in the range 2.006(2)–2.225(3) Å (avg. 2.162 Å), comparable to those in $Sb_2O(O_3PCH_2PO_3)$ [1.927(2)–2.396(2)] (11) and several

TABLE 3
Selected Bond Lengths (Å) and Angles (deg) for 1

Sb(1)–O(4A)	2.006(3)	Sb(1)–O(3)	2.178(2)
Sb(1)–O(1A)	2.225(3)	P(1)–O(2)	1.509(2)
P(1)–O(1)	1.536(3)	P(1)–O(3)	1.540(2)
P(1)–C(1)	1.839(3)		
O(4A)–Sb(1)–O(3)	81.50(10)	O(1A)–Sb(1)–O(1C)	84.99(15)
O(3)–Sb(1)–O(3B)	85.45(13)	O(4A)–Sb(1)–O(1A)	79.77(9)
O(3)–Sb(1)–O(1A)	91.74(10)	O(3)–Sb(1)–O(1C)	161.28(10)
C(1)–O(4)–Sb(1D)	111.5(3)	P(1)–O(1)–Sb(1D)	114.53(14)
P(1)–O(3)–Sb(1)	136.89(15)		

Note. Symmetry transformations used to generate equivalent atoms: A: $x, y, z-1$; B: $x, -y+\frac{3}{2}, z$; C: $x, -y+\frac{3}{2}, z-1$; D: $x, y, z+1$.

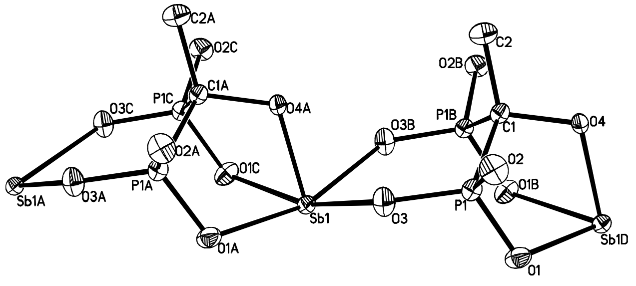

FIG. 1. A fragment of the $[Sb\{CH_3C(O)(PO_3)_2\}]_n^{2n-}$ chain in structure **1** with the atomic labeling scheme (thermal ellipsoids shown at 50% probability).

other antimony(III) phosphate compounds (20, 21). The O–Sb–O bond angles of compound **1** are normal. The Sb atoms are chelated and bridged by $\{CH_3C(O)(PO_3)_2\}^{5-}$ ligand with the formation of a linear chain along the *c* direction. Each phosphonate group of $\{CH_3C(O)(PO_3)_2\}^{5-}$ is related to the other by a mirror plane. The P–O distances range from 1.509(2) to 1.540(2) Å, while the O–P–O bond angles range from 107.86(16) to 113.45(16)°, in agreement with those of other metal-hedp compounds (9, 13).

The neighboring $[Sb\{CH_3C(O)(PO_3)_2\}]_n^{2n-}$ chains are separated by the $[NH_3(CH_2)_4NH_3]^{2+}$ cations (Fig. 2). Hydrogen bonds are formed between the nitrogen atoms of the diamine and the phosphonate oxygens. The N(1)…O(2), N(1)…O(2)^{i} and N(1)…O(3)^{ii} (symmetry code: i, $-x+\frac{3}{2}$, $-y+1$, $z+\frac{1}{2}$; ii, x, y, $z+1$) distances are 2.713(4), 2.878(4), and 2.981(4) Å, respectively. Compound **2** is isostructural to compound **1**, indicated by their powder XRD patterns (Fig. 3), except that the $[NH_3(CH_2)_5NH_3]^{2+}$ in **2** replaces the $[NH_3(CH_2)_4NH_3]^{2+}$ cation in **1**.

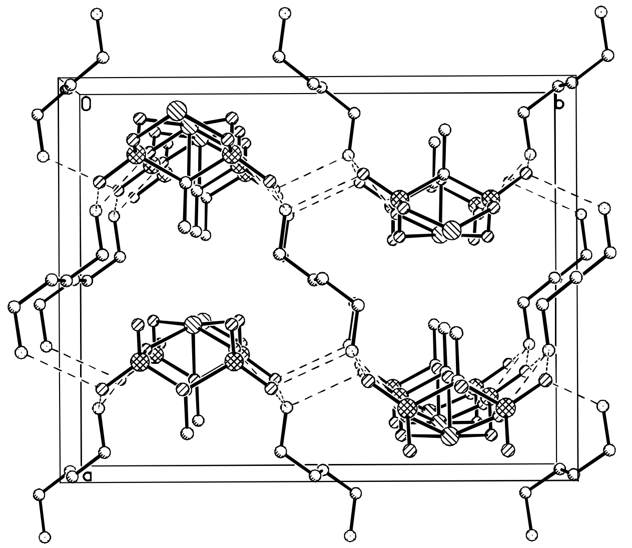

FIG. 2. Crystal packing of compound **1** viewed approximately normal to the crystallographic *ab* plane. The hydrogen atoms are omitted for clarity.

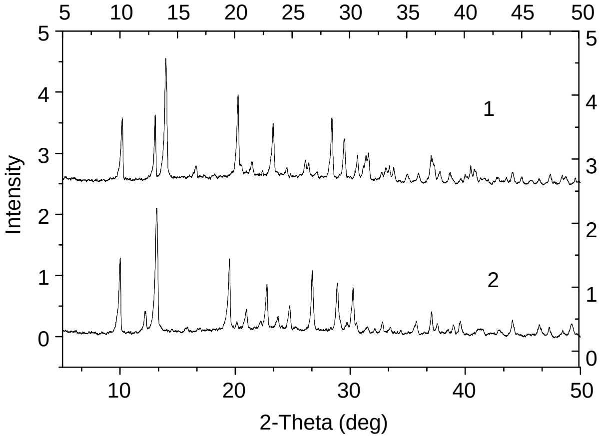

FIG. 3. The X-ray diffraction patterns of compounds **1** and **2**.

The chain structure of compound **1** is different from that of $Sb_2O(O_3PCH_2PO_3)$ (11), where a three-dimensional network structure is observed. The difference originates from the coordination modes of the diphosphonate ligands in the two cases. In compound **1**, the $\{CH_3C(O)(PO_3)_2\}^{5-}$ acts as a bis(chelating) ligand, using four of its six phosphonate oxygens and one hydroxy oxygen, and bridges the Sb atoms into a chain. In compound $Sb_2O(O_3PCH_2PO_3)$, however, five phosphonate oxygens of $\{O_3PCH_2PO_3\}^{4-}$ are each coordinated to one Sb atom, thus resulting in a network structure. Consequently, the coordination environment around Sb is distorted octahedral in **1**, while it is a distorted trigonal bipyramid in $Sb_2O(O_3PCH_2PO_3)$.

The structure of compound **1** may be compared with some transition metal compounds with the same diphosphonate ligand. In $[NH_3(CH_2)_nNH_3]M_2(\text{hedpH})_2 \cdot 2H_2O$ ($M =$ Fe, Zn; $n = 4, 5$) (22, 23), the hedpH^{3-} also serves as a bis(chelating) bridging ligand to link the metal ions into an infinite single chain. Two single chains are further fused together through edge-sharing of the $\{MO_6\}$ octahedra, forming a double chain. In compound **1**, however, the presence of a lone pair electron blocks the formation of a similar double chain. As a result, only a single chain is observed.

Thermal Analyses and IR Spectra

Thermal analyses revealed that compounds **1** and **2** are stable until about 320°C. A single-step decomposition is observed for both **1** and **2** between 325 and 550°C. The weight losses (25.4% for **1**, 28.8% for **2**) are higher than those calculated for the removal of the organic diamines (21.8% for **1**, 26.8% for **2**), suggesting the collapse of the lattice structure. The infrared spectra of the two compounds exhibit a series of bands in the 1000–1150 cm^{-1} range, corresponding to the vibrations of phosphonate

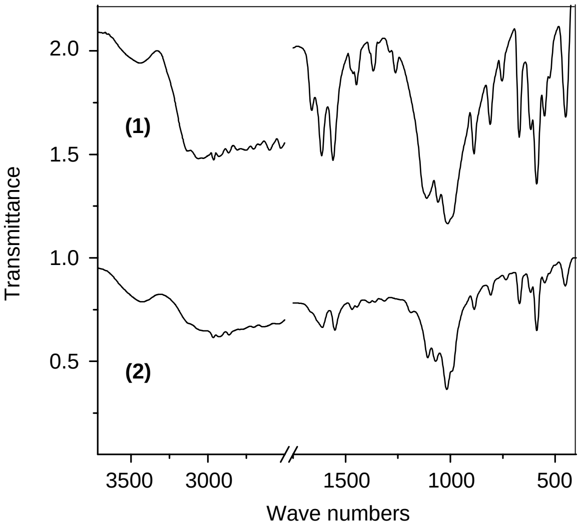

FIG. 4. IR spectra for compounds **1** and **2**.

PO_3 groups (Fig. 4). The broad bands at 2600–3100 cm^{-1} are due to the presence of extensive hydrogen bonds between diammonium nitrogens and the phosphonate oxygens.

In summary, this paper reports two new antimony(III) diphosphonate compounds $[NH_3(CH_2)_nNH_3][Sb\{CH_3C(O)(PO_3)_2\}]$ ($n = 4$, 5) synthesized under hydrothermal conditions. They exhibit a unique linear chain structure, built up from the distorted $\{SbO_5E\}$ octahedra and $\{CPO_3\}$ tetrahedra.

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