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PAPER

Tetranuclear stiboxanes $(RSb)_4O_6$, exhibiting an adamantane-type structure†

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Depolymerization reactions of organostibonic acids with protic ligands have been investigated. Reaction of arylstibonic acids with 8-hydroxyquinoline (8-HQ), or {2-[1*H*-pyrazol-5(3)-yl]naphthalene-1-ol} (H_2naphpz) in a 1 : 1 stoichiometry in refluxing toluene affords adamantane-like $L_4(RSb)_4O_6$ clusters [(*p*-$XC_6H_4Sb)_4(O)_6(Q)_4$] (where X = Cl (**1**), Br (**2**), QH = 8-hydroxyquinoline), [(*p*-$ClC_6H_4Sb)_4(O)_6$-(Hnaphpz)$_4$]·H_2naphpz (**3**) and [(*p*-Br-$C_6H_4Sb)_4(O)_6$(Hnaphpz)$_4]_2$·H_2naphpz (**4**). Further a tetrameric organoantimony oxo cluster, $L_4(RSb)_4O_4$ [(*p*-$ClC_6H_4Sb)_4(O)_4$(naphpz)$_4$] (**5**) has also been isolated as a side product in the reaction of arylstibonic acid with naphthylphenolic pyrazole. Interestingly **1–4** structurally resemble the dimeric form of the antimony oxide Sb_2O_3 and its mineral senarmontite.

Introduction

Synthesis and structural characterization of discrete molecular oxo clusters is an area of active research as clusters are believed to be the linkers between molecules and materials and help in understanding the size-related properties of materials.[1] Though metal oxides have been found to be useful in numerous catalytic processes,[2] their insolubility in common organic solvents due to their polymeric nature limits their potential applications and the understanding of the chemistry involved with such systems. In such cases, interaction of oxides with organic ligands proves to be an efficient method as it helps in solubilizing the oxides providing a better insight into their solid-state structures and hence their properties.[3]

The use of antimony oxides as fire retardants[4] and in catalysis[5] has been well known for decades. In comparison, the chemistry of organostibonic acids is much less explored despite potential applications of organoantimony compounds in catalysis[6] and biology.[7] Very recently, organostibonic acids have been shown to bind specifically to B-ZIP proteins at micromolar concentrations, thereby inhibiting their DNA binding capability and hence could be used as potential anticancer agents.[8] Despite these applications, due to the amorphous and powdery nature of organostibonic acids, their solid-state structure has been a matter of debate.[9] In this regard, a report by Beckmann *et al*. on the structure of the first molecular aryl stibonic acid using bulky substituents on antimony needs special mention.[10] Another interesting report in the chemistry of organostibonic acids is their ability to act as inorganic cryptands incorporating transition metals in their cavity.[11] Further, depolymerization reactions of organostibonic acids with protic ligands like organosilanediols,[12] phenolic pyrazoles[13] and the utility of mixed antimonate–phosphonate clusters as pro-ligands for synthesizing 3d clusters have also been reported.[14] Self-condensation reactions of organostibonic acids in the presence of bases have been investigated leading to the isolation of novel nonanuclear,[15] dodecanuclear[16,17] and hexadecanuclear isopolyoxostibonates.[13] It should also be mentioned here that though chemistry of monoorganostibonic acids is less investigated, several di- and triorganoantimony oxo clusters have been synthesized and structurally characterized by Sowerby and Breunig *et al*.[18]

In our continued effort to understand the reactivity of organostibonic acids with various protic ligands and to have a better insight in to the basic structural units involved in organoantimony oxo clusters, reactions of organostibonic acids with 8-hydroxyquinoline and naphthylphenolic pyrazole has been studied. Details of the synthesis along with the single crystal X-ray structural characterization of the products obtained are presented in this manuscript.

Results and discussion

Reaction of arylstibonic acid (aryl = *p*-ClC_6H_4, *p*-BrC_6H_4) with 8-hydroxyquinoline in a 1 : 1 stoichiometry was carried out in refluxing toluene for 6 h. Evaporation of the solvent followed by crystallization in toluene at room temperature yielded pale yellow/colourless crystals in moderate yields (Scheme 1). The products were characterized by standard analytical and spectroscopic techniques.

Crystals suitable for single crystal X-ray diffraction were grown in a week by slow evaporation of toluene. The solid-state structures of **1** and **2** were found to be isostructural, hence the structure of **1** (Fig. 1) is considered only for discussion. Compound **1** crystallizes in tetragonal space group $I4_1/a$. The structure of **1** is a highly symmetric adamantyl core consisting of antimony and oxygen atoms. Each Sb atom lies at the vertex of

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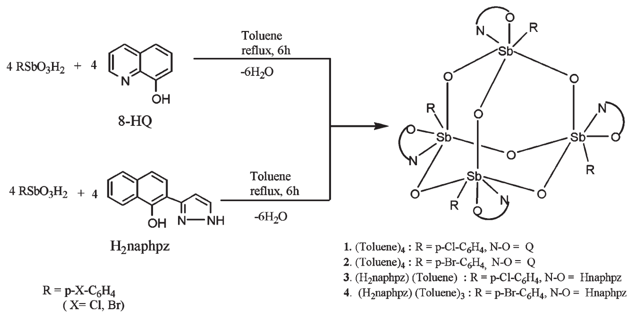
† Electronic supplementary information (ESI) available: ORTEP for **2** and **4** and supramolecular interactions for the compounds **3** and **4** are provided. CCDC 808827–808831. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30587a



Scheme 1

Table 1 Bond length and bond angle comparison between senarmontite and compounds **1–4** (average bond parameters are given)

	Bond length (Å)	Bond angles (°)	
Compound	Sb–O	Sb–O–Sb	O–Sb–O
Senarmontite	1.977	132.50	95.60
1	1.944	130.50	96.43
2	1.936	130.20	96.57
3	1.976	130.76	96.09
4	1.946	130.83	96.19

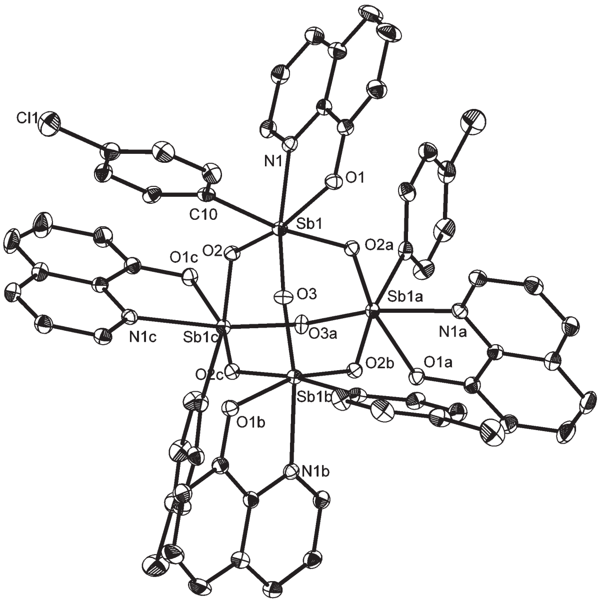


Fig. 1 Molecular structure of **1** with thermal ellipsoids shown at 30% probability.

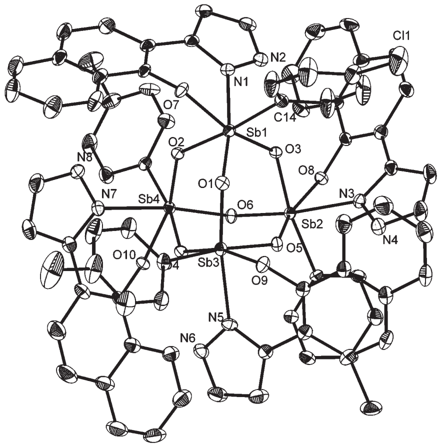


Fig. 2 Molecular structure of **3** with thermal ellipsoids shown at 30% probability. A molecule of free ligand and solvent (toluene) that co-crystallized with **3** have been removed for clarity.

the tetrahedron with the oxygens at the edges forming an Sb_4O_6 framework. The ligand chelates to the Sb atom through the O,N-donor site forming a slightly puckered 5-membered ring. Each Sb atom is in an octahedral site with O4NC coordination mode. The Sb–O bond distances and the angles (Sb–O–Sb and O–Sb–O) are 1.944 Å, 130.50° and 96.43° respectively. Interestingly the bond parameters in **1** and **2** are very similar to the ones found in senarmontite which is summarized in (Table 1).

Further reactions of arylstibonic acid (aryl = *p*-ClC_6H_4, *p*-BrC_6H_4) with H_2naphpz[19] in 1 : 1 stoichiometry were carried out in refluxing toluene and the products were crystallized in toluene by slow evaporation (Scheme 1). Single crystal X-ray structural elucidation of **3** and **4** revealed the formation of an adamantane-type structure similar to **1** and **2**. The clusters **3** and **4** crystallize in monoclinic space group $P2_1/n$ and triclinic space group $P\bar{1}$ respectively. A free ligand molecule co-crystallized along with compound **3** (Fig. 2) in the asymmetric unit, where as in compound **4** two independent adamantane-like molecules and a free ligand molecule crystallized in the asymmetric unit. The ligand (O,N,N-donor) chelates to the metal atom through an O,N-mode resulting in the formation of a six-membered ring while the other nitrogen of the pyrazole ring remains essentially non-coordinating. The Sb–O bond distances and the angles (Sb–O–Sb and O–Sb–O) are 1.946 Å, 130.83° and 96.19° respectively. The observed bond parameters again fall in the range as in the mineral senarmontite. A closer look in to the crystal structure of **3** revealed interesting N–H⋯O and N–H⋯π supramolecular interactions (ESI†). Of the N–H⋯O interactions observed in **3**, four are intramolecular N–H⋯O and one is intermolecular. The intramolecular bond parameters fall in the range 2.479–2.573 Å with the bond angles ranging from 106.2–108.5°. For the intermolecular $N_{10}H\cdots O1$ interaction, the observed bond distance and angle are 2.199 Å and 146.0° respectively. For the N–H⋯π (of electron-rich oxyphenyl) interactions observed in **3**, the bond lengths fall in the range from 2.740 to 2.802 Å with the bond angles ranging from 155.9–162.6°. It should be noted that a similar kind of N–H⋯O and N–H⋯π interactions are also observed in **4** (ESI†). For the N–H⋯O interaction the bond distances range from 2.470–2.655 Å with the bond angles ranging from 102.8–109.7°. Similarly for the N–H⋯π (of electron-rich oxyphenyl) interaction, the observed bond distances and angles fall in the range 2.530–3.169 Å and 153.5–164.4° respectively.[20]

The formation of the Sb_4O_6 adamantane-type framework is interesting considering the fact that the dimeric form of Sb_2O_3 and its mineral senarmontite are built up of similar frameworks. Though adamantane-type structures are known for metal oxides like As_4O_6 in the solid state,[21] similar structures for Bi_4O_6 have been proposed as neutral species only in the gas phase.[22] So far

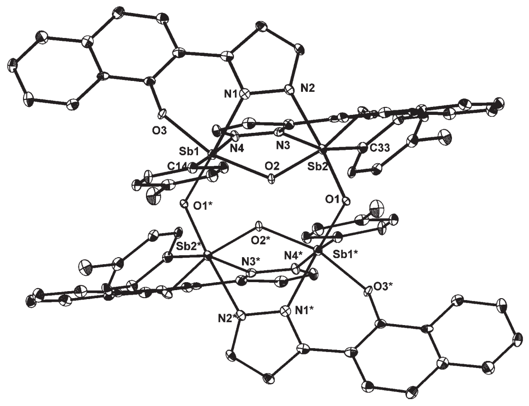


Fig. 3 Molecular structure of **5** with thermal ellipsoids shown at 30% probability.

as main group metal-oxo clusters are concerned, adamantane-type structures are a rarity, though they are quite common in transition metal chemistry.[23] Though adamantane-type M_4O_6 clusters are reported for main group metals like aluminium,[24] gallium,[24] indium[25] and tin,[26] with respect to antimony there are no reports on such framework though Sb_4O_6 non-adamantane-type clusters are known. The closest structurally related molecular compound is a cage compound $MeC(CH_2SbO)_3$ which consists of a six-membered Sb_3O_3 ring with the rest of the adamantane core made of carbons.[26b] It has to be mentioned here that an adamantane-like cluster has been proposed as a possible alternative structure for a product resulting from the reaction of organoantimony halides with dicyclohexyl phosphinic acid.[27]

The molecular structures (**1–4**) also have close resemblance to the recently isolated unusual natural polyarsenic compound Arsenicin A, from the New Caledonian sponge *Echinochalina bargibanti*.[28] A recent report on the chemical synthesis and the single crystal X-ray structure elucidation of Arsenicin A is significant considering its potential application as bacterial and fungicidal activities on human pathogenic strains.[29] **1–4** can be considered as high oxidation state antimony analogues of Arsenicin A, with three CH_2 groups in the polyarsenic compound replaced by oxygens.

Compound **5** crystallizes in triclinic space group $P\bar{1}$ as a side product along with **3** in small quantities (Fig. 3). Structural elucidation revealed the formation of a tetranuclear organoantimony oxo cluster similar to the product isolated on reaction of arylstibonic acids with phenolic pyrazoles which we have reported recently.[13] In **5** the ligand binds to the metal atoms through both a chelating (O,N-donor) as well as bridging mode (N,N-donor). It is of interest to mention here that the adamantane-type structure which forms initially can lose two molecules of water leading to the formation of the tetranuclear organoantimony-oxo cluster (eqn (1)). In fact an independent experiment was carried out by refluxing **3** in toluene for 6 h and a Dean–Stark apparatus was used to remove the water molecules formed in the course of the reaction as an azeotropic mixture.

$$[(p\text{-Cl-}C_6H_4Sb)_4(O)_6(HnaPhpz)_4] \xrightarrow{-2H_2O} [(p\text{-Cl-}C_6H_4Sb)_4(O)_4(naPhpz)_4] \quad (1)$$

The reaction mixture was cooled to room temperature and the solvent was evaporated to yield a colourless product. Standard analytical and spectroscopic techniques revealed that the colourless product was **3** and not **5** as expected. Even using an organic dehydrating agent like phthalic anhydride could not convert **3** to **5**.

Conclusion

In summary, we report the formation of an unprecedented Sb_4O_6 adamantane-type framework for the first time in antimony-based molecular metal-oxo clusters, which can be considered as structural analogues of the mineral senarmontite. Currently reactions of organostibonic acids with various other protic ligands are being explored in an attempt to stabilize novel structural forms based on Sb–O frameworks.

Experimental section

General procedures

Solvents, 8-hydroxyquinoline and common reagents were purchased from commercial sources, whereas *p*-halophenylstibonic acids and phenolic pyrazole were synthesized using literature procedures.[9,19] Infrared spectra were recorded on a JASCO-5300FT-IR spectrometer as KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis was performed on a Flash EA Series 1112 CHNS analyser. Compounds **1–5** lose solvent of crystallization rapidly. Hence the isolated crystals were powdered and subjected to high vacuum for 1 h before elemental analysis and NMR were taken. Hence the signals corresponding to solvent of crystallization toluene do not appear in the ^1H and ^{13}C NMR spectra. Similarly the elemental analysis also shows a solvent-free CHN analysis report. Further ^1H and ^{13}C NMR spectra are not reported for compounds **1** and **2** owing to poor solubility in common organic solvents.

General synthetic method

p-Halophenylstibonic acid and the ligand (8-HQ or H_2naphpz) were taken in 1 : 1 stoichiometry in 50 ml toluene and refluxed for 6 h using a Dean–Stark apparatus to remove water eliminated in the reaction as an azeotropic mixture. The clear solution that was obtained was cooled to room temperature and were filtered. Molar ratios and weights of reactants used are as follows.

Compound 1. *p*-Chlorophenylstibonic acid (0.35 g, 1.23 mmol) and 8-HQ (0.18 g, 1.23 mmol). Crystals suitable for single crystal X-ray diffraction were obtained by the diffusion method using filtrate/hexane over the course of a week. Yield of isolated crystals: 0.20 g (40.80% based on *p*-chlorophenylstibonic acid). Dec. temp: 240 °C. IR (cm^{-1}, KBr pellet): 3057 w, 2959 w, 1601 m, 1575 m, 1498 s, 1462 s, 1377 m, 1323 m, 1261 s, 1107 m, 796 s, 518 m, 486 m. Elemental analysis: found: C, 44.73; H, 2.46; N, 3.51. Calc. for $C_{60}H_{40}N_4O_{10}Cl_4Sb_4$: C, 44.87; H, 2.51; N, 3.48%.

Table 2 X-ray data collection parameters for **1–5**

	1	**2**	**3**	**4**	**5**
Formulae	$C_{88}H_{72}Cl_4N_4O_{10}Sb_4$	$C_{88}H_{72}Br_4N_4O_{10}Sb_4$	$C_{96}H_{70}Cl_4N_{10}O_{11}Sb_4$	$C_{186}H_{138}Br_8N_{18}O_{21}Sb_8$	$C_{90}H_{64}Cl_4N_8O_8Sb_4$
F_w, g mol^{-1}	1974.30	2152.14	2168.42	4574.42	2014.29
Cryst syst	Tetragonal	Tetragonal	Monoclinic	Triclinic	Triclinic
Cryst size, mm	0.20 × 0.16 × 0.10	0.22 × 0.14 × 0.10	0.24 × 0.18 × 0.12	0.22 × 0.16 × 0.12	0.24 × 0.18 × 0.12
Space group	$I4_1/a$	$I4_1/a$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	19.4622(10)	19.226(9)	20.029(10)	17.3569(12)	11.1209(9)
b, Å	19.4622(10)	19.226(9)	21.285(10)	21.1518(14)	11.5866(10)
c, Å	20.882(10)	21.370(19)	21.577(10)	24.9421(17)	17.2087(14)
α, °	90.0	90.0	90.0	79.6580(10)	83.2620(10)
β, °	90.0	90.0	95.200(7)	85.4730(10)	81.3270(10)
γ, °	90.0	90.0	90.0	76.5070(10)	69.8120(10)
v, Å^3	7909.8(10)	7899(9)	9161(7)	8753.0(10)	2052.3(3)
Z	4	4	4	2	1
D_{calcd} Mg m^{-3}	1.658	1.810	1.572	1.736	1.630
T, K	100	100	100	100	100
μ, mm^{-1}	1.550	3.440	1.349	3.113	1.495
$F(000)$	3920	4208	4304	4472	996
θ range, °	1.43 to 25.08	1.42 to 25.13	1.35 to 25.00	1.21 to 25.00	1.20 to 25.00
No. of. refln colled	36 644	26 764	84 836	84 882	19 965
Completeness to θ max (%)	99.6	99.7	100.0	99.7	99.8
No. of. indep refln/R_{int}	3503/0.032	3472/0.047	16 131/0.091	30 737/0.032	7219/0.054
GooF (F^2)	1.068	1.070	1.084	1.062	1.109
R_1 (F) ($I > 2\sigma(I)$)	0.028	0.050	0.048	0.037	0.048
wR_2 (F^2) (All data)	0.076	0.144	0.119	0.100	0.103
Largest diff peak/hole, e Å^{-3}	1.080/−0.591	2.237/−1.289	1.295/−0.682	2.955/−3.023	1.39/−1.038

Table 3 Bond length (Å) and bond angle (°) parameters for compounds **1–3**

1		**2**		**3**	
Sb1–O1	2.065(2)	Sb1–O1	2.046(5)	Sb1–O1	1.951(3)
Sb1–O2	1.948(19)	Sb1–O2	1.933(4)	Sb1–O2	1.948(3)
Sb1–O3	1.938(13)	Sb1–O3	1.933(3)	Sb1–O3	1.960(3)
Sb1–N1	2.238(2)	Sb1–N1	2.222(6)	Sb1–O7	2.024(3)
Sb1–C10	2.133(3)	Sb1–C10	2.114(7)	Sb1–N1	2.206(4)
Sb1–O2a–Sb1a	132.88(10)	Sb1–O2a–Sb1a	132.70(2)	Sb2–O5	1.958(3)
Sb1–O3–Sb1b	125.93(14)	Sb1–O3–Sb1b	126.00(5)	Sb2–O6	1.939(3)
O2–Sb1–O2a	92.15(7)	O2–Sb1–O2a	92.73(16)	Sb2–O8	2.017(3)
O2–Sb1–O3	103.99(8)	O2–Sb1–O3	93.67(17)	Sb2–N3	2.196(4)
C10–Sb1–O2	92.31(10)	C10–Sb1–O2a	92.20(2)	Sb3–O4	1.945(3)
C10–Sb1–N1	89.7(10)	C10–Sb1–N1	89.60(2)	Sb3–O9	2.012(3)
				Sb3–N5	2.196(4)
				Sb4–O6	1.931(3)
				Sb4–O2	1.957(3)
				Sb4–O10	2.017(3)
				Sb4–N7	2.192(4)
				Sb1–C14	2.116(5)
				Sb1–O3–Sb2	132.72(17)
				Sb1–O1–Sb3	126.38(16)
				Sb1–O2–Sb4	133.66(16)
				O1–Sb1–O2	91.11(13)
				O2–Sb1–O3	92.17(12)
				O2–Sb4–O6	102.36(13)
				O2–Sb1–O7	86.54(12)
				O5–Sb3–O4	91.59(12)
				O7–Sb1–N1	79.10(14)
				N1–Sb1–C14	92.52(17)
				C14–Sb1–O3	91.83(16)

Compound 2. *p*-Bromophenylstibonic acid (0.40 g, 1.22 mmol) and 8-HQ (0.17 g, 1.22 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by the diffusion method using filtrate/hexane over the course of a week. Yield of isolated crystals: 0.20 g (37.0% based on *p*-bromophenylstibonic acid). Dec. temp: 245 °C. IR (cm^{-1}, KBr pellet): 3061 w, 2964 m, 1604 m, 1577 m, 1498 s, 1460 s, 1377 m, 1325 m, 1261 s, 1093 m, 800 s, 482 m. Elemental analysis: found: C, 40.38; H, 2.21; N, 3.09. Calc. for $C_{60}H_{40}N_4O_{10}Br_4Sb_4$: C, 40.40; H, 2.26; N 3.14%.

Table 4 Bond length (Å) and bond angle (°) parameters for compounds **4–5**

4		**5**	
Sb1–O1	1.941(3)	Sb1–O2	1.953(3)
Sb1–O2	1.945(3)	Sb1–O1*	1.933(3)
Sb1–O3	1.957(3)	Sb1–N1	2.146(4)
Sb1–O7	2.024(3)	Sb1–C14	2.117(5)
Sb1–N1	2.197(3)	Sb1–O3	2.000(3)
Sb2–O5	1.954(3)	Sb1–N4	2.141(4)
Sb2–O6	1.932(3)	Sb2–O1	1.948(3)
Sb2–O8	2.029(3)	Sb2–O2	1.943(3)
Sb2–N3	2.213(4)	Sb2–O4	1.992(3)
Sb3–O1	1.932(3)	Sb2–N2	2.264(4)
Sb3–O4	1.946(3)	Sb2–N3	2.116(4)
Sb3–O9	2.025(3)	Sb1–O2–Sb2	120.82(17)
Sb3–N5	2.207(3)	Sb2–O1–Sb1*	131.96(18)
Sb4–O6	1.943(3)	O1–Sb2–O2	95.82(14)
Sb4–O10	2.009(3)	O1*–Sb1–O2	99.73(14)
Sb4–N7	2.210(3)	O2–Sb1–N4	85.11(15)
Sb1–C14	2.129(4)	O1*–Sb1–O3	93.14(14)
Sb1–O2–Sb2	132.52(16)	O3–Sb1–N1	81.86(15)
Sb1–O3–Sb4	133.67(14)	C14–Sb1–O2	94.34(17)
Sb1–O1–Sb3	127.30(15)		
Sb4–O4–Sb3	133.99(15)		
O1–Sb1–O2	91.69(12)		
O2–Sb1–O3	92.64(12)		
C14–Sb1–N1	88.82(15)		
O3–Sb4–O4	91.71(12)		
O2–Sb1–O7	85.51(12)		
O7–Sb1–N1	79.07(13)		

Compound 3. *p*-Chlorophenylstibonic acid (0.35 g, 1.23 mmol) and H_2naphpz (0.26 g, 1.23 mmol). Colorless crystals were isolated over the course of a week by slow evaporation of filtrate (toluene). Yield: 0.24 g (37.5% based on *p*-chlorophenylstibonic acid). Dec. temp: 260 °C. IR (cm^{-1}, KBr pellet): 2961 w, 1624 w, 1562 m, 1473 m, 1388 m, 1261 s, 1087 s, 1016 m, 887 m, 804 s, 486 m. ^1H NMR (400 MHz, $CDCl_3$) a broad signal at δ: 8.98 ppm (–OH), δ 6.90–8.59 ppm (m) for aromatic protons; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.88, 149. 80, 149.29, 134.90, 134.56, 134.16, 129.14, 128.83, 127.84, 127.73, 127.34, 126.53, 125.73, 125.45, 125.20, 124.77, 122.99 ppm. Elemental analysis: found: C, 51.36; H, 3.12; N 6.65. Calc. for $C_{89}H_{62}N_{10}O_{11}Cl_4Sb_4$: C, 51.48; H, 3.01; N, 6.74%.

Compound 4. *p*-Bromophenylstibonic acid (0.35 g, 1.06 mmol) and H_2naphpz (0.22 g, 1.06 mmol). Colorless crystals were isolated over the course of a week by slow evaporation of filtrate (toluene). Yield: 0.26 g (45.3% based on *p*-bromophenylstibonic acid). Dec. temp. 270 °C. IR (cm^{-1}, KBr pellet): 2962 w, 1633 w, 1562 m, 1475 m, 1390 m,1261 s, 1086 s, 1022 m, 885 m, 802 s, 478 m. ^1H NMR (400 MHz, $CDCl_3$) a broad signal at δ 9.20 ppm (–OH), δ 6.74–8.62 ppm (m) for aromatic protons; ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.95,149.26, 134.91,134.44, 130.58, 129.05, 128.79, 127.81, 127.30, 126.54, 125.64, 125.46, 125.31, 125.18, 124.78, 123.98, 123.03 ppm. Elemental analysis: found: C, 46.17; H, 2.58; N, 5.79. Calc. for $C_{165}H_{114}Br_8N_{18}O_{21}Sb_8$: C, 46.11; H, 2.67; N, 5.87%.

Compound 5. Obtained as a side product along with **3**. Yield: 0.12 g (21.2% based on *p*-chlorophenylstibonic acid) Dec. temp: 280 °C. IR (cm^{-1}, KBr pellet): 3341 m, 3055 w, 1664 w, 1562 s, 1527 s, 1473 m, 1390 m, 1253 m, 1224 m, 1136 m, 1084 s, 1006 m, 887 m, 808 m, 773 m, 729 m, 609 m, 580 m, 480 m. ^1H NMR (400 MHz, $CDCl_3$) δ: 6.87–7.91 ppm (m) for aromatic protons. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.84, 150.51, 149.23, 134.91, 134.46, 130.53, 129.05, 128.75, 128.24, 127.77, 127.31, 126.54, 126.02, 125.59, 125.31, 124.80, 122.91, ppm. Elemental analysis: found: C, 49.71; H, 2.51; N, 6.15. Calc. for $C_{76}H_{48}N_8O_8Cl_4Sb_4$: C, 49.88; H, 2.64; N, 6.12%.

X-ray crystallography

Important crystal data parameters are given in Table 2. Selected bond lengths and bond angles for **1–5** are given in Tables 3 and 4. Single crystal X-ray data collection for **1–5** were carried out at 100(2) K on a Bruker Smart Apex CCD area detector system (λ(Mo Kα) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINTPLUS. The structures were solved using SHELXS-97 and refined using SHELXS-97.[30] All non-hydrogen atoms were refined anisotropically. Some of the structures have residual electron density owing to solvent of crystallization which could not be properly fixed. In compound **1**, solvent of crystallization toluene molecules were constrained to be hexagonal using the AFIX 66 command. In compounds **3**, **4** and **5**, solvent voids were noticed but we were unable to locate the corresponding solvent of crystallization. These solvent contributions were removed by the SQUEEZE[31] command in the PLATON program. In compound **4**, the residual electron density is also due to a heavily disordered bromine atom (Br_2) which has not been modeled.

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