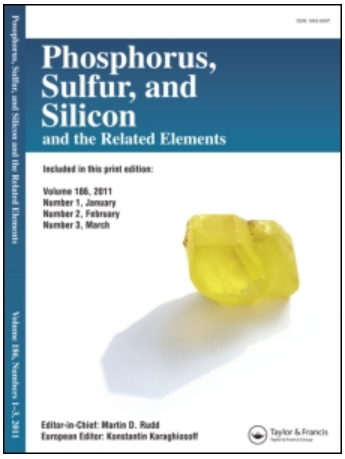

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Ring and Chain Systems in Structures of Organo Antimony(III) and Bismuth(III) Halides

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Alkylantimony (III) and -bismuth(III) halides, R_2EX, REX_2, (E = Sb, Bi; X = Cl, Br, I) tend to form oligomeric or polymeric structures through halogen bridges between the pnicogen atoms. In this article the crystal structures of several examples with sterically more ($R = (Me_3Si)_2CH$) or less ($R = CH_3$) demanding organic substituents are discussed.

Keywords: antimony; bismuth; halogen compounds; coordination polymers

INTRODUCTION

It is well known that organo antimony(III) and bismuth(III) halides are valuable reagents for the syntheses of organometallic pnicogen ring compounds. Homocycles, $(RSb)_n$ [1], $(RBi)_n$ [2] and heterocycles $(RSbE)_n$, (E = O [3], S, Se, Te [4]) are formed by reactions of $RSbX_2$ or $RBiX_2$ (X = Cl, Br) with Mg/THF or Na_2E (E = chalcogen) respectively. Recent examples are the cyclobismuthanes, R_nBi_n (R =

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$(Me_3Si)_2CH$, n = 3, 4) [2]. Not only the reactivity but also the structural chemistry of the title compounds is related to inorganic ring systems. Due to the Lewis amphoteric nature of these compounds there is a strong tendency to form coordination oligomers or polymers through halogen bridges between the pnicogen atoms. The resulting molecular structures include infinite linear chains (e.g., $(CH_3)_2SbI$ [5], $(Me_3Si)_2CHBiCl_2 \cdot 0.5Et_2O$[6],dimers ($(Me_3Si)_2CHBiCl_2$·tetrahydrofuran [7]), chains of rings (CH_3EX_2, E = Sb ; X = Cl [8], Br [8], I [9]; E = Bi, X = I [10]) or two dimensional layers (CH_3BiCl_2) [11].

RESULTS AND DISCUSSION

Crystals of dimethylantimony iodide consist of pyramidal $(CH_3)_2SbI$ molecules which are aligned to bent chains through short intermolecular Sb···I contacts trans to the Sb-I bonds. The structure of the chain is depicted in Figure 1.

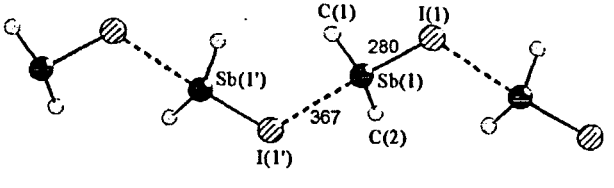


FIGURE 1 Structure of the $[(CH_3)_2SbI\cdots]_x$ chains in the crystal structure of dimethylantimony iodide; distances in pm, angles I(1)-Sb(1)···I(1')171.87(4)°, Sb(1)···I(1')-Sb(1') 116.83(4)°

A characteristic feature of the structure of $(Me_3Si)_2CHBiCl_2$·tetrahydrofuran (Figure 2) is the central four membered Bi_2Cl_2 heterocycle formed by association of two molecular units.

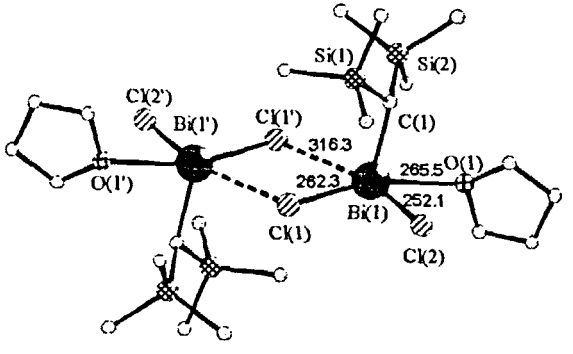
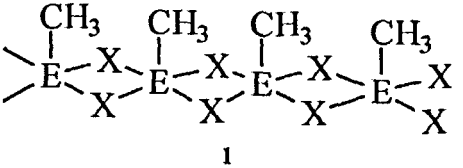


FIGURE 2 Structure of $(Me_3Si)_2CHBiCl_2$·tetrahydrofuran, distances in pm, angles Bi(1)-Cl(1)-Bi(1') 105.70(11) ° Cl(1)-Bi(1)-Cl(1') 74.30(1) °

The structures of CH_3EX_2 (E = Sb ; X = Cl, Br, I ; E = Bi, X = I) consist of four membered heterocycles aligned to chains through shared vertices (1).



1

In contrast, the crystal structure of CH_3BiCl_2 consists of puckered monolayers of CH_3Bi units and Cl atoms arranged in a four connected net. A view on a monolayer of CH_3BiCl_2 is depicted in Figure 3.

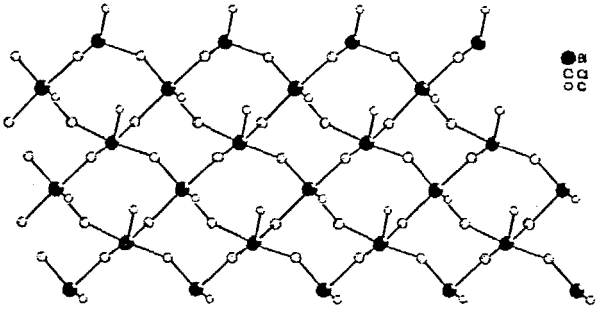


FIGURE 3: View on a monolayer in the structure of CH_3BiCl_2, bond lengths Bi-Cl 274.11(15); 275.53(13) pm

Common features in the structures of both, $(CH_3)_2SbI$ and CH_3EX_2 (E = Sb, X = Br, I; E = Bi, X = Cl, I) imply the association of the chains or monolayers respectively through weak pnicogen···halogen contacts with formation of a sequence of inorganic and organic double layers in the crystals.

Attempts to obtain single crystals of CH_3BiBr_2 have not been successful. The solubility of this dibromide in noncoordinating solvents is very poor. Crystallisation from a solution in tetrahydrofuran gives crystals of the complex $CH_3BiBr_2 \cdot 2$ tetrahydrofuran. The structure of this complex contains distorted square pyramidal molecules which are associated to dimers (Figure 4).

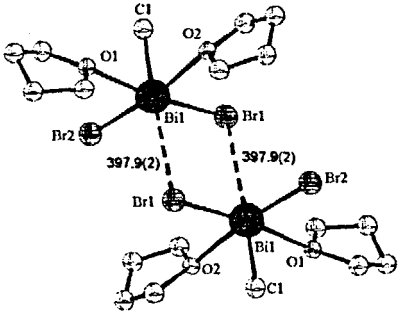


FIGURE 4. Dimeric units in the crystal structure of $CH_3BiBr_2 \cdot 2$tetrahydrofuran, distances (pm) Bi-C 223.5 ; Bi-O 260.4; 264.2; Bi-Br 270; 271.4; angles (°) C-Bi-Br 93.51, C-Bi-Br 91.7.

Acknowledgments

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