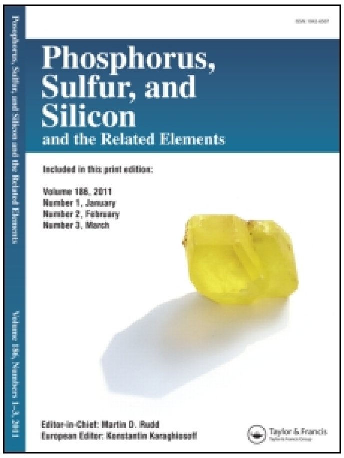

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UPON SOME INORGANIC HETEROCYCLES IN THALLIUM (I) BORATES AND GERMANATES

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The structural study of some hydrated thallium (I) borates shows the existence of *macroionic chains* which can be considered as condensed heterocycles. In Tl $[B_3O_4(OH)_2]$ $0.5H_2O$, the unit is the well known B_3O_3 ring; it is formed by two BO_3 triangles (Δ) and one BO_4 tetrahedron (T); these units are linked to form an infinite chain; its shorthand notation is $3:\infty^1$ $(2\Delta + T)$. The structure of Tl_4 $[B_7O_{10}(OH)_3 \cdot OBO(OH)]$ H_2O contains a unit constituted by three B_3O_3 rings linked together by *boron atoms*; each ring is formed by two BO_4 tetrahedra and one BO_3 triangle; the corresponding fully hydrated polyanion is $[B_7O_9(OH)_7]^{4-}$. The chain is made up of units linked by $BO_2(OH)$ triangles; the shorthand notation of this borate is: $7:\infty^1$ $[(3\Delta + 4T) + \Delta]$.

The structure of $Tl_8Ge_5O_{14}$ is composed of isolated Ge_5O_{14} units; they are formed by a crown of four GeO_4 tetrahedra linked by shared oxygens; two other oxygens of two of these GeO_4 tetrahedra belong also to a fifth GeO_4 tetrahedron which is located at the center of the crown.

In the general study of the oxygenated thallium (I) compounds, we paid attention to borates[1-10] and germanates.[11,12] The crystal structure determinations enabled us to show the existence of chains or isolated units which may be included in inorganic heterocycles as they were defined by Professor Garcia-Fernandez.[13]

I. HYDRATED BORATES

1) In the hydrated triborate, $Tl[B_3O_4(OH)_2]0.5H_2O$,[7] the polyanion is a chain made up of the well known B_3O_3 heterocycles (Figure 1). This compound agrees with the structural classification of borates proposed by Christ and Clark;[14] this one is based on the existence of fundamental building blocks (FBB) which, in borates, are found isolated or form, by linkage, chains, sheets or three-dimensional networks. So, the shorthand notation of this triborate is $3:\infty^1$ $(2\Delta + T)$ ($\Delta = BO_3$ triangle; $T = BO_4$ tetrahedron).

2) The second compound studied is a hydrated diborate $Tl_4[B_8O_{12}(OH)_4]H_2O$.[8] The borate ion is a chain made up of units formed by eight boron atoms (Figure 2); the FBB existing in these units is different of those previously described.[14,15] In this borate, a new FBB with seven boron atoms is found (Figure 3). The shorthand notation is $7:\infty^1$ $[(3\Delta + 4T) + \Delta]$; the linkage between two blocks is made by a $BO_2(OH)$ triangle, B(8) in Figure 2.

In Figure 4, we have reported the known units of two hydrates of thallium (I) diborate: $Tl_2[B_4O_6(OH)_2]2H_2O$,[16] *a* and $Tl_4[B_8O_{12}(OH)_4]H_2O$, *b*; their shorthand notations are respectively $3:\infty^1$ $[(\Delta + 2T) + \Delta](16)$ and $7:\infty^1$ $[(3\Delta + 4T) + \Delta]$. It can be noted on Figure 4 that the *b* ion is the dimer of the *a* ion (9). Another hydrate of thallium (I) diborate exists, $Tl_2B_4O_7H_2O$;[1] its structure could contain chains made up of units described in Figure 4c (10); the structural formula could be

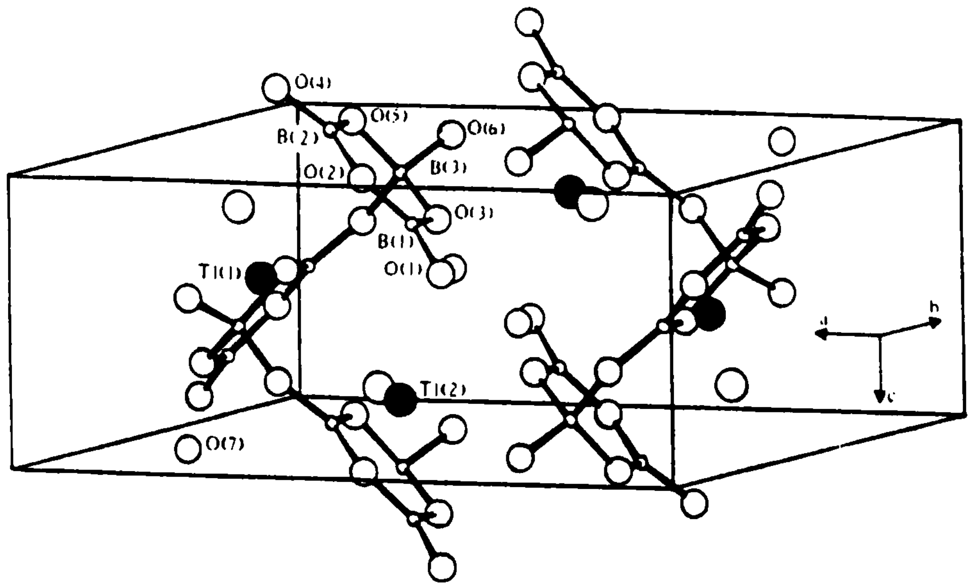

FIGURE 1 Crystal structure of Tl $[B_3O_4(OH)_2]$ $0.5H_2O$.

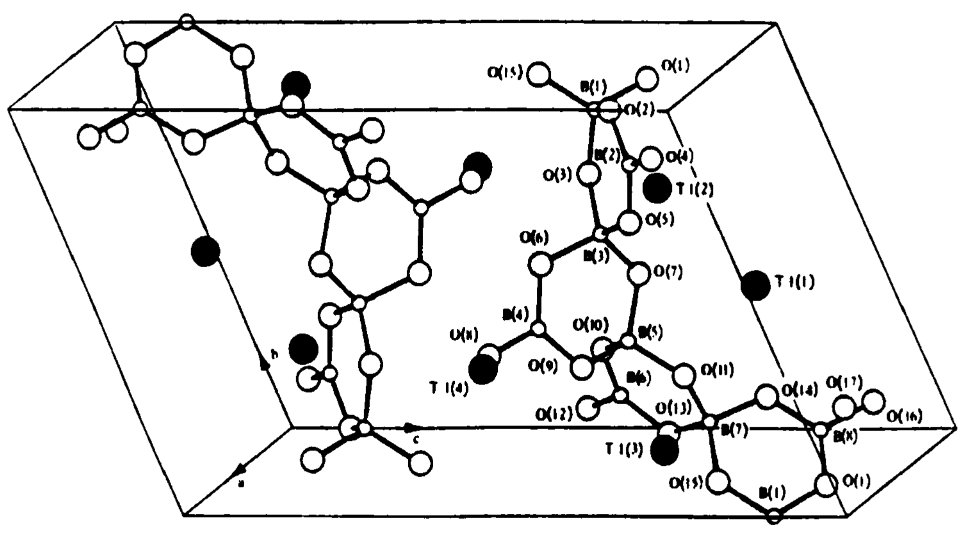

FIGURE 2 Crystal structure of Tl_4 $[B_8O_{12}(OH)_4]$ H_2O.

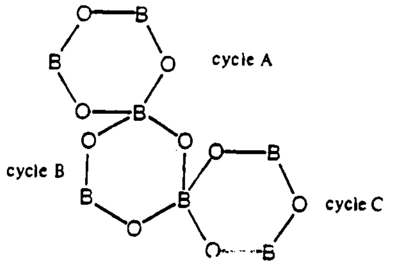

FIGURE 3 Fundamental building block with seven boron atoms.

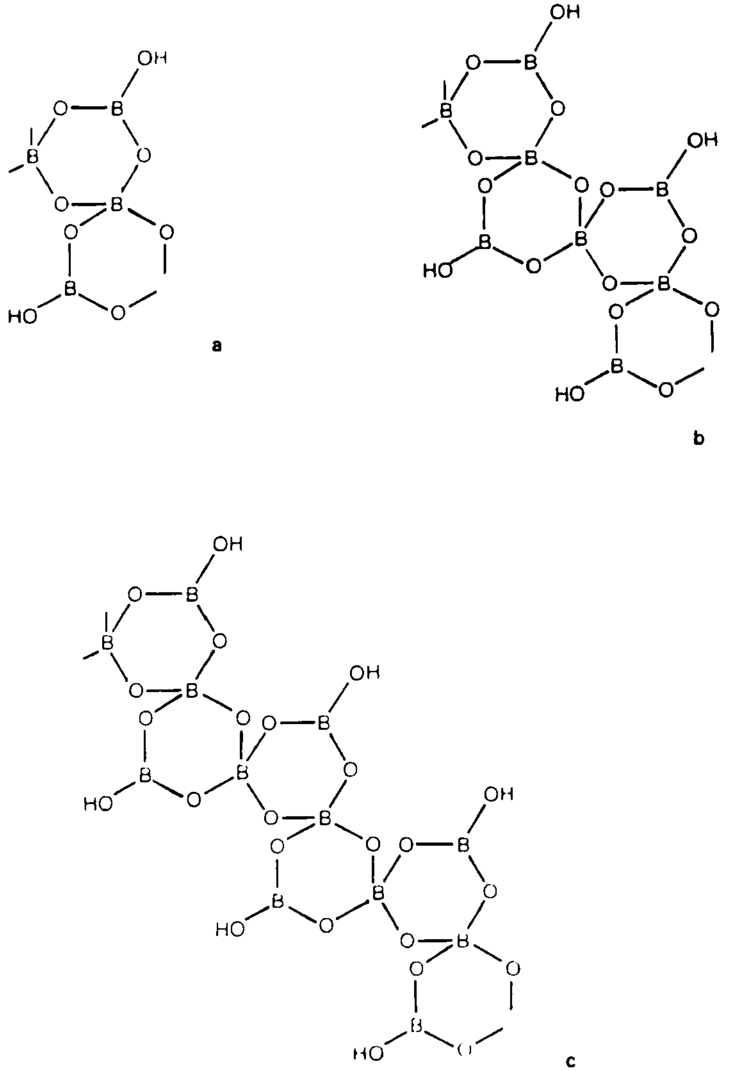

FIGURE 4 Units of the chains in the hydrates of thallium (I) diborate: $Tl_2B_4O_7 \cdot 3H_2O$, $Tl_2B_4O_7 \cdot 1.5H_2O$ and $Tl_2B_4O_7 \cdot 1H_2O$

$Tl_6[B_{12}O_{18}(OH)_6]$ where the *c* ion is the trimer of *a* ion. A new FBB with eleven boron atoms could exist in this borate: $11 : \infty^1$ $[(5\Delta + 6T) + \Delta)]$. This hypothesis has not been confirmed by structural determination because no crystal has been obtained. Nevertheless, a few arguments may be put forward to support this hypothesis. The percent water has been determined by chemical and thermogravimetric analysis and also by the study of the binary system $H_2O—Tl_2B_4O_7$.[10] The very simple powder diagram of this compound may be indexed in a hexagonal lattice; its experimental density corresponds to three $Tl_2B_4O_7 \cdot H_2O$ in a cell which agrees with the structural formula $Tl_6[B_{12}O_{18}(OH)_6]$.

II. THE $Tl_8Ge_5O_{14}$ GERMANATE[11]

The formula of this compound has been established by structure determination. It is constituted of isolated units Ge_5O_{14} which consist of five GeO_4 tetrahedra linked by some vertices (Figure 5). Four GeO_4 tetrahedra, joined by two vertices form a crown and the fifth GeO_4 tetrahedron is located at the center of the crown; it is linked with two symmetrical GeO_4 tetrahedra. An isostructural thallium (I) silicate $Tl_8Si_5O_{14}$ has been synthesized.[12] Ge_5O_{14} and Si_5O_{14} heterocycles have never been reported before.

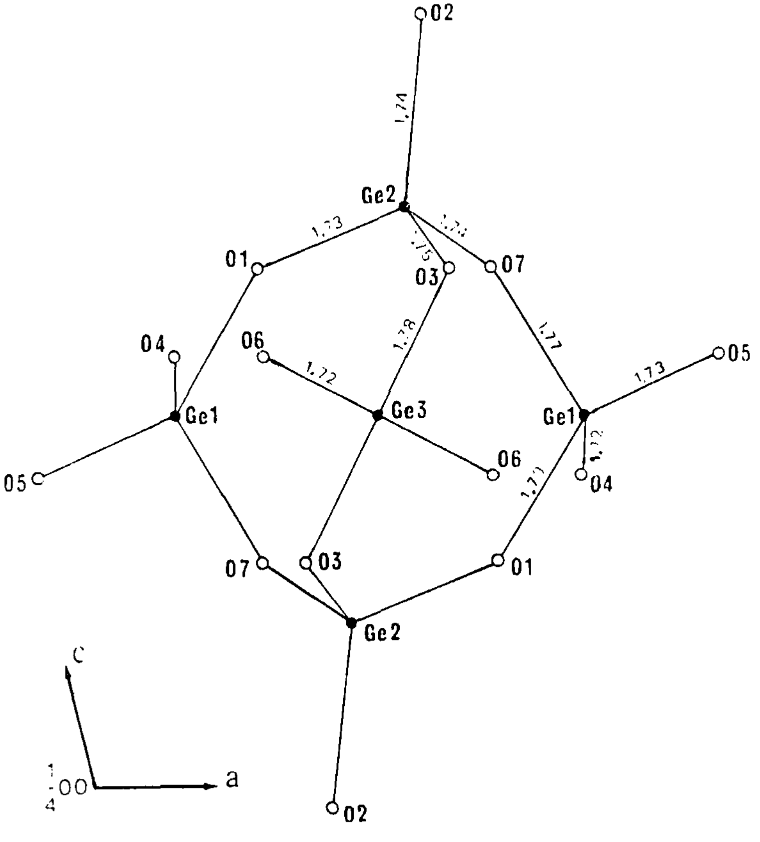

FIGURE 5 Isolated unit Ge_5O_{14} in $Tl_8Ge_5O_{14}$ (Ge—O bond lengths in Å).

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