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ORIGINAL RESEARCH PAPER

NEW ORGANO-AND HALOTIN (IV) WITH EDTA: SYNTHESIS AND INFRARED STUDY

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Abstract: Nine acidic or neutral ethylenediaminetetraacetato [H_2Y^{2-}, H_3Y^- or Y^{4-}] containing adducts and derivatives have been synthesized and studied by infrared. The suggested structures are discrete with octahedral or trigonal bipyramidal environments around the tin centres, the ethylenediaminetetraacetic anion behaving as a bidentate and hydrogen bonds involved, a tridentate, a tetradentate, a bichelating and hydrogen bonds involved ligand, a tri- or tetrachelating ligand. For all the structures when intermolecular hydrogen bonds involving OH or CH groups are considered, a supramolecular architecture may be obtained.

Keywords: *bidentate and hydrogen bonds involved, tridentate, tetradentate, bichelating and hydrogen bonds involved, a tri-, tetrachelating ethylenediaminetetraacetic anion, discrete structures, hydrogen bonds, supramolecular architectures*

INTRODUCTION

The interesting structural aspects and applications in organotin(IV) chemistry-medicine, agriculture, industry - explain the interest of various research groups worldwide [1-4]. In the framework of our research work in the coordinating ability of oxyanions towards organotin (IV) molecules, our group has yet published some papers [5-10] and report here the study of the interactions between $[Et_4N][H_3Y]\cdot 3H_2O$ or $[BzN(CH_3)_2[H_2Y]\cdot H_2O$ and $SnPh_3Cl$, $SnBu_2Cl_2$ or $SnCl_2\cdot 2H_2O$which has yielded nine new compounds, infrared study of which have been carried out then structures suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

$[Et_4N][H_3Y]\cdot 3H_2O$ (L_4) and $[BzNMe_3]_2[H_2Y]\cdot H_2O$ (L_5) have been obtained as powders after the water evaporation of the solution obtained on dissolving ethylenediaminetetraacetic acid (EDTA) in aqueous solutions of Et_4NOH or $BzNMe_3OH$ in 1 : 4 ratio. The analytical data % calculated (%found): (L_4): C = 45.46(46.07), H = 8.69(8.75), N = 8.84(8.88); (L_5): C = 59.19(59.07), H = 7.95(7.87), N = 9.20(9.23) have allowed to suggest the above formulae for (L_4) and (L_5). When $SnPh_3Cl$ or $SnBu_2Cl_2$ are allowed to react with (L_4) and (L_5) in ethanol in specific ratios, white precipitates are obtained which are stirred around two hours and washed with ethanol: $SnBu_2Cl_2$ with L_5 in 4 : 1 ratio gives (**A**); $SnPh_3Cl$ with L_5 in 2 : 1 ratio gives (**B**); $SnPh_3Cl$ with L_4 in 4 : 1 ratio gives (**C**); $SnBu_2Cl_2$ with L_4 in 4 : 1 gives (**D**); $SnPh_3Cl$ with L_4 in 2 : 1 ratio gives (**E**). The analytical data have allowed to suggest the following formulae % calculated (%found): $[BzNMe_3]_2[H_2Y]\cdot 3SnBu_2Cl_2$

(**A**): C = 43.17(43.20), H = 6.71(6.80), N = 3.73 (3.70); $H_2Y(SnPh_3)_2\cdot 2H_2O$

(**B**): C = 55.79(55.72), H = 4.48(4.60), N = 2.83(2.78); $[Et_4N][H_3Y]\cdot 3SnPh_3Cl$

(**C**): C = 52.64(52.70), H = 5.35(5.26), N = 2.79(2.72); $[SnBu_2][H_2Y]\cdot 2SnBu_2Cl_2\cdot 4H_2O$

(**D**): C = 33.95(33.82), H = 6.37(6.47), N = 2.33(2.40); $Y(SnPh_2)_2$

(**E**): C = 48.96(48.82), H = 3.87(3.81), N = 3.36 (3.30).

When $SnCl_2$ is allowed to react with (L_4) or (L_5) in specific ratios, white precipitates are obtained which are stirred around two hours and washed with ethanol:
- $SnCl_2$ with L_4 in 5 : 1 ratio gives (**F**);
- $SnCl_2$ with L_4 in 1 : 2 ratio gives (**G**);
- $SnCl_2$ with L_4 in 2 : 1 ratio gives (**H**);
- $SnCl_2$ with L_5 in 5 : 1 ratio gives (**I**).

The analytical data have allowed to suggest the following formulae % calculated (%found): $SnY\cdot 3SnCl_2(OH)_2\cdot 2EtOH\cdot H_2O$

(**F**): C = 14.15(14.05), H = 02.72(02.79), N = 02.36(02.42);
$SnY\cdot 5SnCl_2(OH)_2\cdot EtOH.5H_2O$

(**G**): C = 08.67(08.74), H = 02.04(02.17), N = 01.68(01.67);
$SnY\cdot 2SnCl_2(OH)_2\cdot\frac{1}{2}EtOH\cdot 2H_2O$

(**H**): C = 14.76(14.60), H = 02.36(02.47), N = 03.13(03.27);$[BzNMe_3\cdot Cl]_2[BzNMe_3\cdot OH]_2\cdot SnY\cdot 4SnCl_2(OH)_2\cdot 6H_2O$

(**I**): C = 28.39(27.96), H = 04.67 (04. 67), N = 03.97 (03.83).

The infrared spectra were recorded with a Bruker FTIR (4400 -350cm^{-1}) spectrometer at Saint Boniface College, Winnipeg-Canada. The elemental analyses have been performed at the laboratory of Microanalyses - University of Bath (UK) -. Infrared data are given in cm^{-1} - abbreviations: (br) broad, (vs.) very strong, (s) strong, (m) medium, (sh) shoulder. All the chemicals are from Aldrich Company –Germany-and were used without any further purification.

RESULTS AND DISCUSION

Let us consider the infrared data of the studied derivatives based on assignments in [11] $\nu_{as}COO$+ δNH (1647sh-1625s), δCH_2+ $\nu_s COO$ (1425sh-1375s), νCC (818sh) for (**A**);

$\nu_{as}COO$+ δNH (1638s-1559sh), δCH_2+ $\nu_s COO$ (1486m-1340sh), νCC (919sh), $\nu SnPh_3$(728-696)vs for (**B**);

$\nu_{as}COO$ +δNH (1648s-1559w), δCH_2+ $\nu_s COO$ (1480m-1456s), $\nu SnPh_3$(718-676)vs, νCC (967w) for (**C**);

νOH_2+ νNH (3435)s, $\nu_{as}COO$+δNH (1668s), δCH_2+ $\nu_s COO$ (1461s-1395sh), νCC (856vs) for (**D**);

$\nu_{as}COO$ (1633s), δCH_2+ $\nu_s COO$ (1480m-1345m), νCC (722sh) for (**E**);

νOH_2(3412s) , $\nu_{as}COO$ (1638s), δCH_2+ $\nu_s COO$ (1435sh-1365s), νCC (718sh) for (**F**);

νOH_2(3602s) $\nu_{as}COO$ (1648s-1549sh), δCH_2+ $\nu_s COO$ (1486m), νCC (909sh) for (**G**);

νOH_2(3432s)$\nu_{as}COO$ (1650s), δCH_2+ $\nu_s COO$ (1482m-1356s), νCC (917w) for (**H**);

νOH_2(3425)s, $\nu_{as}COO$ (1658s), δCH_2+ $\nu_s COO$ (1401s-1355sh), νCC (856vs) for (**I**).

From these data we suggest five discrete structures with the ethylenediaminetetraacetic anion behaving as a bidentate and hydrogen bonds involved, tridentate, tetradentate, bichelating and hydrogen bonds involved, tri or tetrachelating, the environments around the tin centres being octahedral or trigonal bipyramidal.

For **A** a discrete structure with octahedral Sn centres, the anion behaving as a trichelating ligand is suggested (Figure 1).

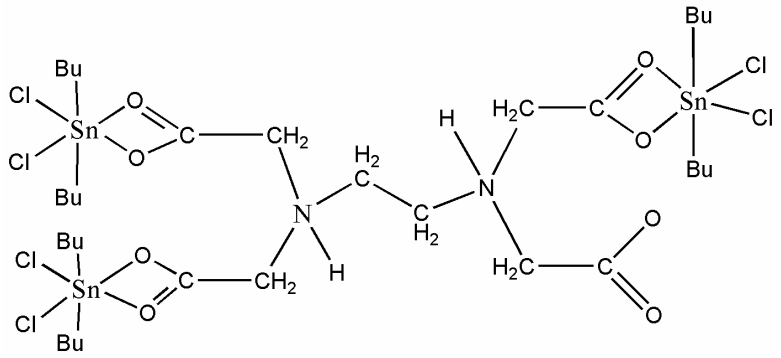

Figure 1. *Proposed structure for the compound* ***A***

For **B** a dimeric structure is suggested with a trigonal bipyramidal environment around Sn centres, the anion behaving as a tetradentate ligand, the water being considered as lattice (Figure 2a) or while considering the water molecules as coordinated ones a

discrete structure with trigonal bipyramidal Sn centres, the anion behaving as a bidentate ligand involved in hydrogen bonding with water molecules (Figure 2b).

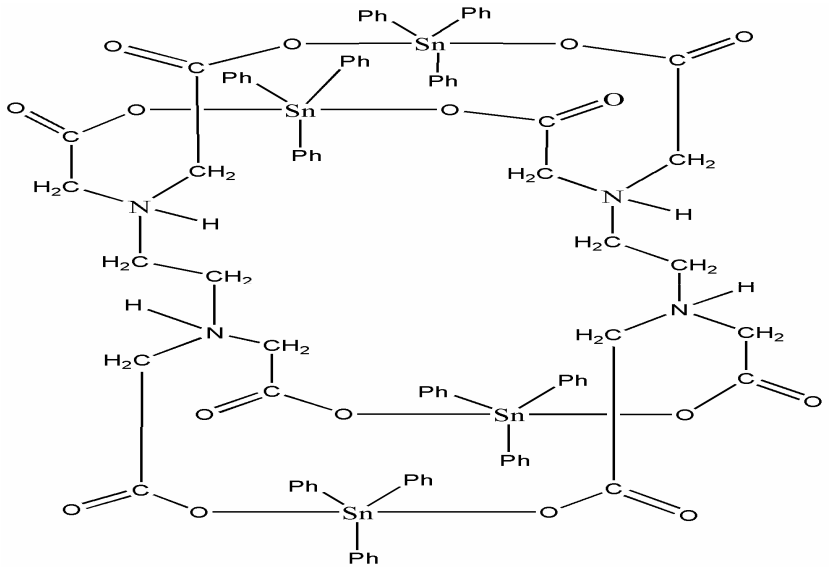

Figure 2a. *Proposed structure for the compound* ***B***

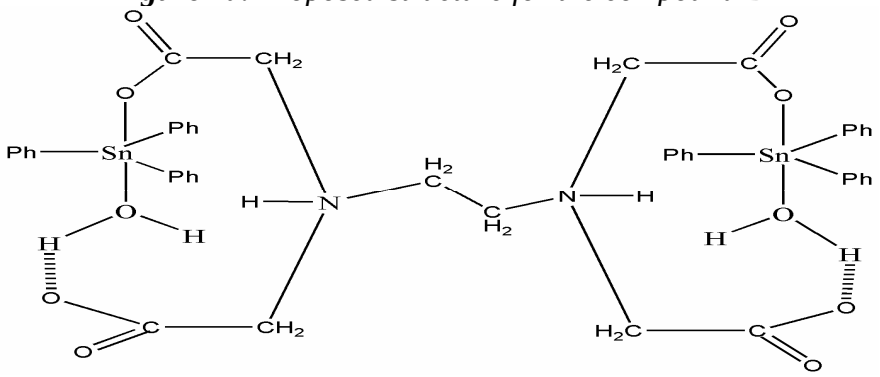

Figure 2b. *Proposed structure for the compound* ***B***

For **C** a discrete structure with Sn centres in a trigonal byramidal environment, the anion behaving as a tridentate ligand (Figure 3).

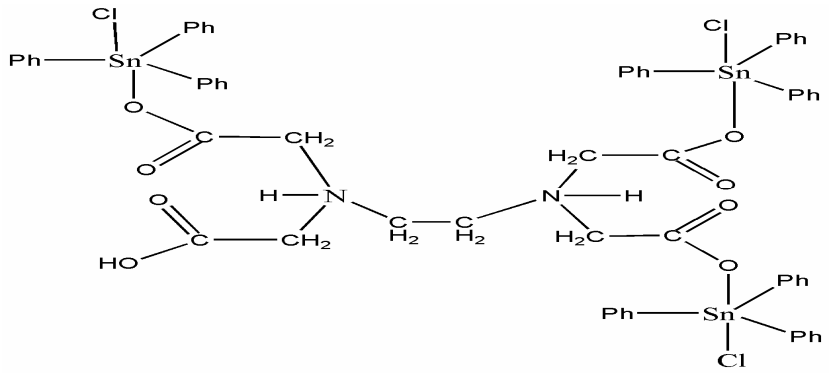

Figure 3. *Proposed structure for the compound* ***C***

The compound **D** contains a $SnBu_2$ residue octahedrally trans coordinated and two $[SnBu_2Cl_2 \cdot 2H_2O]$ adducts connected to the $[SnBu_2 (H_2Y)]$ component through O-----H_2O hydrogen bonds, the anion behaving as a bichelating and hydrogen bonding involved ligand (Figure 4).

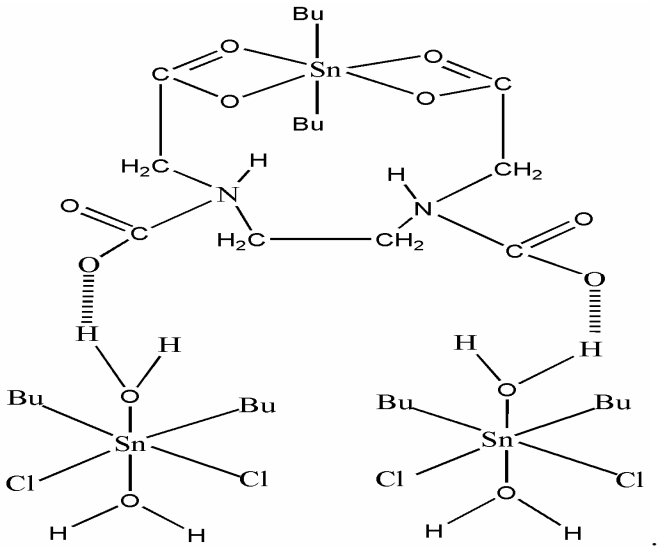

Figure 4. *Proposed structure for the compound* ***D***

For **E** a dimeric structure with Sn centres an octahedral environment, the anion behaving as a tetrachelating ligand (Figure 5).

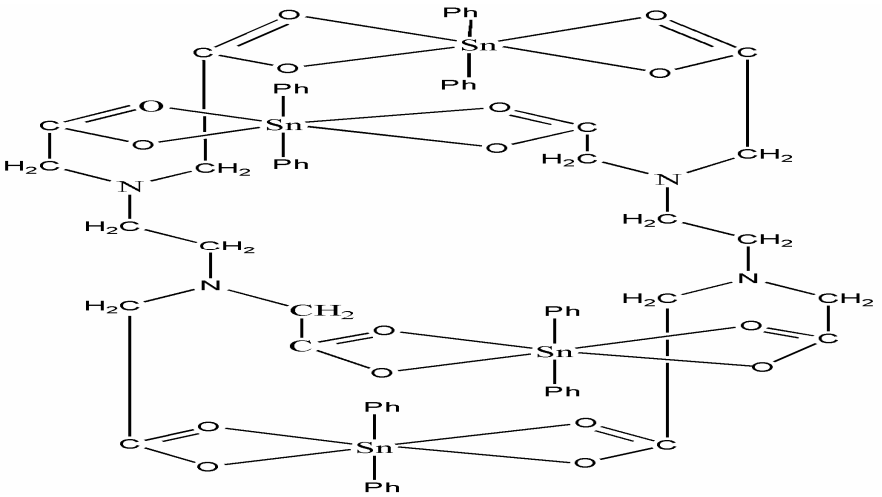

Figure 5. *Proposed structure for the compound* ***E***

The structure of the compound **F** consists of neutral anion pentachelating the central Sn atom and monocoordinating two $[SnCl_2(OH)_2 \cdot EtOH]$ and one $[SnCl_2(OH)_2 \cdot H_2O]$ adducts, the anion behaving as a trichelating and tridentate ligand, the environment around the tin centres being octahedral (Figure 6).

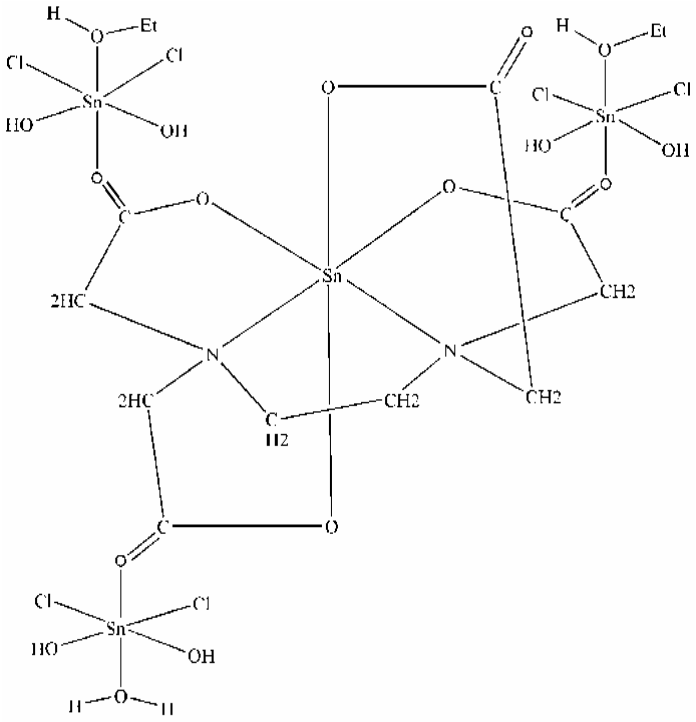

Figure 6. *Proposed structure for the compound* ***F***

For **G** a two components structure is suggested: one component consists of a neutral anion pentachelating the Sn central atom and monocoordinating four $[SnCl_2(OH)_2 \cdot H_2O]$ adducts, the second component being the adduct $[SnCl_2(OH)_2 \cdot EtOH.H_2O]$, the anion behaving as a pentachelating and tetradentate ligand (Figure 7).

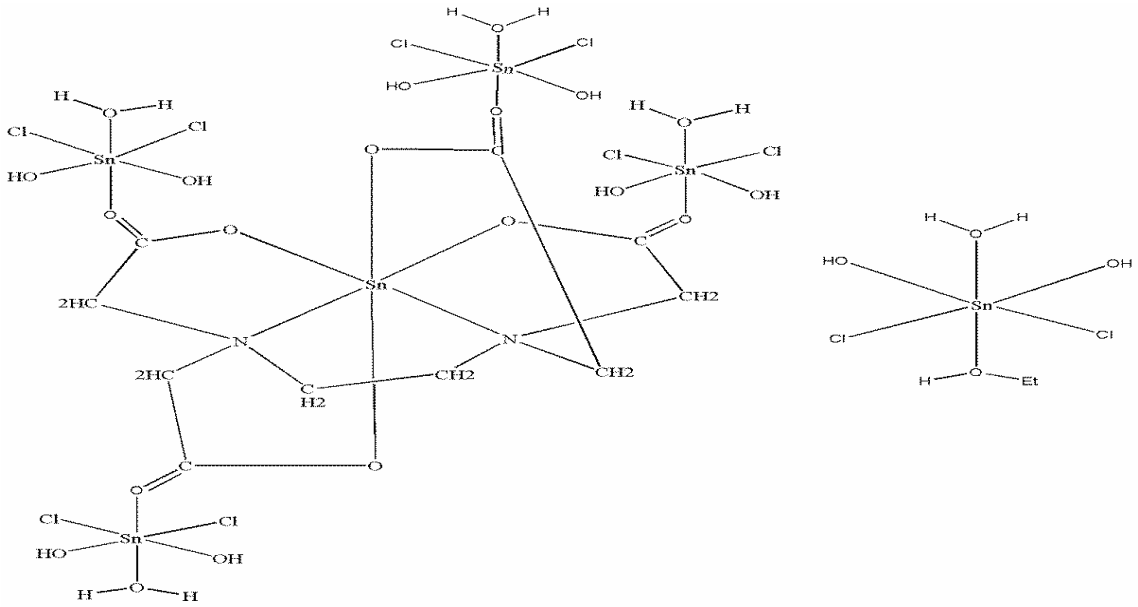

Figure 7. *Proposed structure for the compound* ***G***

The structure of the compound **H** consists of a anion pentachelating Sn central atom and monocoordinating two $[SnCl_2(OH)_2 \cdot H_2O]$ adducts, the anion behaving as a pentachelating and bidentate ligand (Figure 8).

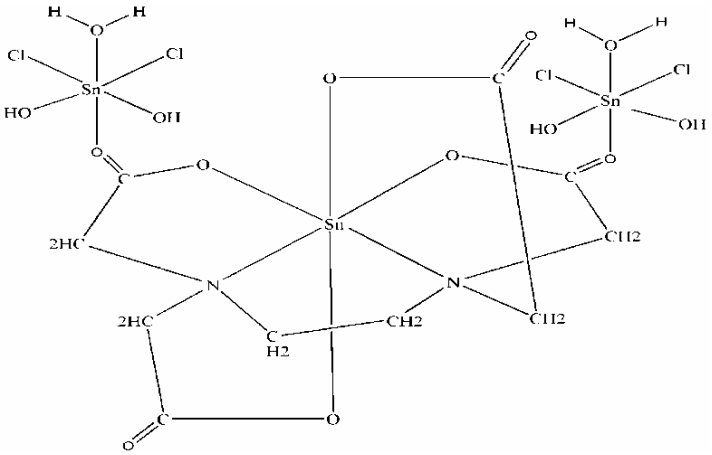

Figure 8. *Proposed structure for compound* ***H***

For **I** the structure consists of a anion pentachelating Sn central atom and monocoordinating two $[SnCl_2(OH)_2 \cdot HO]^-$ and two $[SnCl_3(OH)_2]^-$ complex-anions, the water molecules being lattice, the anion behaving as a pentachelating and tetradentate ligand (Figure 9).

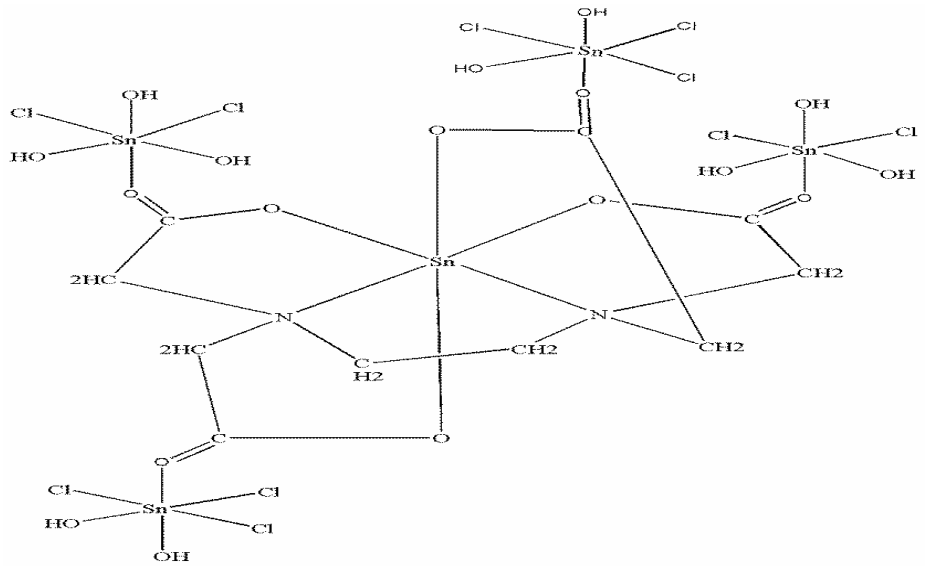

Figure 9. *Proposed structure for compound* ***I***

For all the structures when extra hydrogen bonds are considered supramolecular architectures may be obtained.

CONCLUSION

The structures of five compounds studied in this work have a discrete structure with octahedral or trigonal bipyramidal environments around the tin centres, the anion behaving as a bidentate and hydrogen bonds involved, tridentate, tetradentate, bichelating and hydrogen bonds involved, tri- or tetrachelating ligand. For almost all these structures when intermolecular hydrogen bonds are considered involving OH or CH groups, a supramolecular architecture may be obtained.

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