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Synthesis and Crystal Structure of Potassium Bis(malonato)borate

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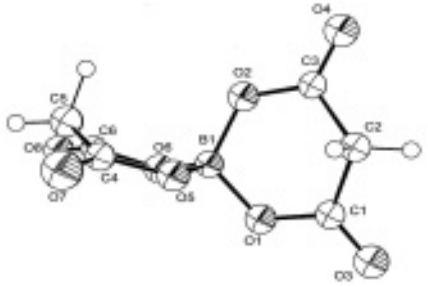
A large number of boric acid bis(chelate) complexes with hydroxy acids are known and they crystal structures have been investigated by X-ray diffraction analysis. The crystal structures of boron coordination complexes with dibasic acids were not carried out. Potassium bis(malonato)borate (I) have been synthesized in anhydrous medium [1]. In order to study the crystal structure we have performed the synthesis of I from a highly concentrated water solution [2]. Well-shaped single crystals of it have been obtained and their full X-ray structural investigation has been carried out.

The structure is formed from K^+ cations and spiran-type complex anions $[(C_3H_2O_2)_2B]^-$. In the complex anion two malonic acid residues are coordinated bidentically to the BO_4-tetrahedron. Bond angles at boron atom vary from 107.4(2)° to 112.5(2)°. The B-O bond lengths being 1.454(2) ÷ 1.472(3) Å. The bond lengths C(sp^2)-O, C(sp^2)=O and C(sp^3)-C(sp^3) are 1.323(3) Å, 1.200(3) Å and 1.505(3) Å in average. The six-membered heterocycles -C-O-B-O-C-C- have the boat conformation. Four atoms of each two heterocycles are coplanar (± 0.024(1) Å), but atom B (-0.370 Å; -0.378 Å) and carbon atoms C(2) (-0.417(1) Å) and C(5) (-0.424(1) Å) are declined from this planes. The oxygen atoms of carbonyl groups O(3), O(4), O(7), O(8) are declined from the main plane of heterocyclic rings to the opposite side to the boron atom. The angles O-B-O, C-C-C, C-O-B and C-C-C in heterocycles amounting to 112.4(2)°, 113.7(2)°, 121.4(2)° and 116.2(2)° in average, respectively. The dihedral angles between the two planes 2C2O of heterocycles is 80.94°. Eight oxygen atoms surround each potassium ion, with K^+-O distances ranging from 2.770(2) to 3.050(3) Å. The infinite chains of potassium polyhedra extend through the crystal almost parallel to the *a* axis. Each coordination polyhedron in the chain posses the mutual edge with two adjacent polyhedrons. Crystals are triclinic, space group $P\bar{1}$: a=7.4071(2), b=7.9160(2), c=9.0752(2) Å; α=113.225(1), β=91.553(1), γ=104.760(2)°; V=467.95(2) Å^3; Z=2; d_x=1.803 g·cm^{-3}; $R1$=0.0405, $wR2$=0.0961 for all 2661 independent reflections.



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Comparison of C-tritylation products of two tricyclic analogs of acyclovir

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Transformation of acyclovir, ACV, a potent antiherpetic drug, into its tricyclic derivative, TACV {1,N^2-ethenoacyclovir; 3,9-dihydro-3-[(2-hydroxyethoxy)methyl]-9-oxo-5*H*-imidazo[1,2-*a*]purine} opens a path to new analogues which are of interest for several reasons. Although TACV itself has only very weak antiviral activity, appropriate substituents at the 6 position of the appended ring may potentiate the activity to a level that is close to that of the parent ACV and make the compounds more selective towards particular herpes viruses. The abovementioned substitutions may simultaneously endow TACV with advantageous physical properties, e.g. a 6-methyl function improves solubility, and 6-aryl groups may confer fluorescence. Substituents at the 6 position also have significant influence on chemical reactivity of the 3,9-dihydro-9-oxo-5-*H*-imidazo[1,2-*a*]purine system of TACV. The treatment of 6-unsubstituted TACV with triphenylmethyl (trityl, Tr) chloride under conditions suitable for regioselective N^5 alkylation, gives a mixture of 5-tritylated and 5,7-ditritylated major products and 7-tritylated minor product. In the case of 6-Ph-TACV, the exclusive formation of 7-[4-(benzhydryl)phenyl]-3,9-dihydro-3-[(2-hydroxyethoxy)methyl]9-oxo-6-phenyl-5*H*-imidazo[1,2-*a*]murine [7-(4-BzhPh)-6-Ph-TACV] is observed.

The unusual 7-Tr-TACV and 7-(4-BzhPh)-6-Ph-TACV C-tritylation products were crystallized and their structures have been determined by single crystal X-ray analysis. In both structures, there is an excess of proton-acceptor groups (N1, N4, O9, O4', O5') over classic proton donors (N5-H, O5'-H). The presence at the C7 position of either a trityl or 4-(benzhydryl)phenyl substituent results in different hydrogen bond interactions and different arrangement of the molecules in the crystal. The O5' hydroxyl group of 7-(4-BzhPh)-6-Ph-TACV accepts a hydrogen bond from the N^5 atom of an inversion-related molecule leading to a centrosymmetric pair of molecules linked by two N5-H...O5' bonds. At the same time, the O5' hydroxyl donates a hydrogen bond to the N1 acceptor and an N5-H ...O5'-H ...N1 cooperative hydrogen bond is formed. This type of intermolecular interactions does not occur in the structure of 7-Tr-TACV, where the dominating role is played by the N5-H...N1 and O5'-H...O5' intermolecular hydrogen bonds.