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CRYSTAL ENGINEERING OF NEW VILOGEN-CONTAINING SUPRAMOLECULAR SYSTEMS: CHAINS VERSUS HELICES ASSIGNED BY H-BONDS

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The semizwitterionic viologens have been synthesized as a new tectones for the crystal engineering of functional materials. It has been shown by the single crystal X-ray diffraction that in contrast to the parent bicationic systems forming anion-bication-anion structure the semizwitterionic viologens could be organized ether as 1-D zig-zag chain or as triple helices depending on the substitutes at nitrogen atoms.

КРИСТАЛІЧНИЙ ДИЗАЙН НОВИХ ВІОЛОГЕНОВМІСНИХ СИСТЕМ: ФОРМУВАННЯ ЛАНЦЮГІВ ТА СПІРАЛЕЙ ЗА РАХУНОК ВОДНЕВИХ ЗВ'ЯЗКІВ

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Синтезовано напівцвіттерійонні віологени як нові тектони для розробки функціональних матеріалів. За допомогою рентгеноструктурного аналізу було показано, що на відміну від споріднених бікатионних систем напівцвіттерійонні віологени можуть бути організовані у лінійні ланцюги та потрійні спіралі в залежності від типу замісників при нітрогенах.

КРИСТАЛЛИЧЕСКИЙ ДИЗАЙН НОВЫХ ВИОЛОГЕНСОДЕРЖАЩИХ СИСТЕМ: ФОРМИРОВАНИЕ ЦЕПЕЙ И СПИРАЛЕЙ ЗА СЧЕТ ВОДОРОДНЫХ СВЯЗЕЙ

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Синтезированы полуцвиттерийонные виологены как новые тектоны для конструирования функциональных материалов. С помощью рентгеноструктурного анализа было показано, что в отличие от родственных бикатионных систем полуцвиттерийонные виологены могут быть организованы в линейные цепи и тройные спирали в зависимости от заместителей при атомах азота.

Viologens (4,4'-bipyridine tertiary salts) are important redox reagents because of their easy and reversible single-electron reduction into the stable and intensely colored radical cations. They are used widely as the electrochromic materials (for example, in electrochromic displays), for electron transfer mediators in conversion of solar energy, for biosensors, matrices of molecular electronic devices etc [1].

In spite that the bipyridine derivatives are quite popular tectons in the crystal engineering [1] of new materials there is no information about the using them in construction of spirals.

At the same time it is well known that a long-chain helices formation is common for the very important natural and natural-like products — nucleic acids, proteins [2], starch [3]. Organization of these substances in the spirals significantly determine their properties. Nevertheless there are only limited number of examples of helices in the synthetic materials [4].

From the other hand it is well known that the one of the most effective method to control the molecules and ions relative positions in crystals is the using of the hydrogen bonds [5]. Therefore in the attempt to

obtain spiral-organized viologen systems we have synthesized 4,4'-bipyridine derivatives containing terminal proton donors and acceptors.

Results and discussion

Semimesoionic viologens 2-[4-(1-carboxymethyl-4-pyridiniumyl)-1-pyridiniumyl]acetate perchloride (**1**) and 3-4-[1-(2-carboxyethyl)-4-pyridiniumyl]-1-pyridiniumylpropanoate perchloride (**2**) with the —COOH and —COO- functional groups have been synthesized from the corresponding dicarboxylic acids [6] by the reaction with 1 equivalent of sodium bicarbonate in water (scheme 1) and the single crystals have been grown by the slow evaporation of their water solutions.

For the such compounds there are two possibilities to form H-bonded associates: centrosymmetric dimer and linear chains formation.

It was found that the compound **1** form infinite chains in crystals assigned by hydrogen bonds (fig. 1).

Bond lengths and angles in the semizwitterionic **1** are virtually the same as the corresponding values in the parent dicationic system **3** (N,N'-bis(2-carboxymethyl)-4,4'-bipyridylium) **7** (scheme 2).

In both reference bicationic compounds (**3** and **4**) all carboxylic hydrogens takes part in the strong H-bonds with anions (O-H ··· Cl and O-H ··· O, accordingly, forming anion-bication-anion structure). That's why such molecules can't be organized in the chained structure like in the semizwitterionic **1** and **2**.

In **2**, as well as in **1**, the central bipyridilium cores are twisted (dihedral angle between pyridine moieties is 17.4°).

Apparently that the strong intermolecular O-H ··· O hydrogen bonds (O ··· O distance 2.474(4) in **1** and 2.452(4) Å in **2**) as well as peculiarities of the molecular structure are the major factors leading to the formation the unusual for viologens crystal packing.

Experimental

Synthesis of viologens **1** and **2**

A solution of sodium bicarbonate (0,2 mmol, 0,0168 g) in 1 ml of water was added to a solution of corresponding dicarboxylic acid (0,2 mmol) in 1 ml of water and allowed to slowly evaporate. Small colourless crystals were obtained.

Crystal structure determination

All crystallographic measurements were performed at the room temperature on a Enraf Nonius CAD4

diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å).

Structures were solved using SHELXS-97 [9] and refined using full-matrix list squares based on F² in SHELXL-97 [10].

In both structures the oxygen atoms of perchlorate anions are disordered over three positions with multiplicity 0.5, 0.35, 0.15 and 0.33*3 respectively. Hydrogen atoms were placed at calculated position. Hydrogen atoms which take part in H-bonds were refined isotropically with constrain O-H distance. The main crystallographic parameters are summarized in Table. Full crystallographic details for **1** and **2** have been deposited at Cambridge Crystallographic Data Centre (CCDC 671854 & 671855 accordingly) .

Conclusions

The semizwitterionic viologens with carboxylic acid terminal groups have been used for the crystal engineering of new systems. It was found that the strong intermolecular O-H ··· O H-bonds is one of the major factors for the ordering these molecules in the twisted *zig-zag* chains. And by tuning the spacer between donor and acceptor (changing the aliphatic chain length) the triple helices have been obtained.

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