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Structural diversity of uranyl complexes with aliphatic monocarboxylate ligands

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In most of the cases interaction between uranyl ions UO_2^{2+} and anions of aliphatic monocarboxylic acids L leads to formation of mononuclear anionic complex units $[\text{UO}_2\text{L}_3]^-$. Crystal structures of corresponding compounds are usually three-dimensional due to electrostatic interactions or hydrogen bonding among the complex ions $[\text{UO}_2\text{L}_3]^-$ and different counter ions. Such compounds have long been studied, especially with acetate ions. However, over the past several years we were able to substantially enlarge the number of uranyl compounds with higher homologues of acetate ion, such as propionate, butyrate and valerate. The results of our synthetic efforts are somewhat surprising. Here we highlight several peculiarities of this family of compounds.

First, there are rare examples of compounds of uranyl ions with anions of aliphatic monocarboxylic acids L constructed of larger heteronuclear clusters. For example, the crystal structure of n-butyrate containing compound $[\text{Sr}(\text{H}_2\text{O})_4[\text{UO}_2\text{L}_3]_2] \cdot 2\text{H}_2\text{O}$ is constructed of trinuclear neutral clusters and the unprecedented neutral octanuclear clusters $\text{K}[\text{UO}_2\text{L}_3]\{\text{R}(\text{H}_2\text{O})_4[\text{UO}_2\text{L}_3]_2\}_2$ were observed in crystal structures of two similar K and Sr or Ba propionates of uranyl ion.

Formation of heteronuclear clusters in the mentioned systems is possible mostly due to the bridging function of anions of aliphatic monocarboxylic acids, which is considered unusual for these ligands. Such coordination mode allows the typical $[\text{UO}_2\text{L}_3]^-$ complex units to bind in larger architectures. According to statistical analysis of the CSD, the bridging function is in fact the most common for butyrate and valerate ions. Thus, even such featureless at the first view monotopic ligands as the ions of aliphatic monocarboxylic acids may facilitate formation of heteronuclear clusters with uranyl ions if other metal atoms except for U are available. This is another curious fact about this family of compounds. Besides, information on the possible and preferred coordination modes of ligands derived in the course of our studies is extremely important for crystal structure prediction and crystal engineering.

The current versions of CSD and ICSD contain respectively about 0.2 and 3.7% of crystal structures featuring cubic crystal system and excluding the inversion center. Curiously and unexpectedly, many uranyl monocarboxylate complexes are noncentrosymmetric and crystallize in cubic crystal system. Noncentrosymmetric crystals may show nonlinear optical (NLO) activity. This third curious fact enhances the value of aliphatic monocarboxylate complexes of uranyl ions and motivated us for the search of new crystals with high NLO activity.

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