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The actinide borates: Inside into nuclear waste storage and new materials for anionic exchange.

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The methods of nuclear fuel vitrification in borate or boroaluminate glasses are very common in nuclear industry. The glasses contain actinides and the products of their decay. For a long time this type of storage of very dangerous components has been described as very safe because of the high kinetic and chemical stability of the borate glasses. Recently, we have found a very easy and efficient method of synthesis of actinide borates. Using a H_3BO_3 flux, we have synthesized several actinyl borates (24 uranyl borates, 4 neptunyl borates, 1 plutonyl and 1 thorium borate). These phases were characterized by X-ray diffraction, spectroscopic and other methods. Several synthesized phases possess unique structural properties, both in actinide chemistry and in chemistry in general. For example, in the structure of Np-borates we have found three different oxidation states (+4, +5 and +6) and three different coordination polyhedra of Np (coordination numbers 6, 7 and 8). The thorium borate (NDTB-1) has a unique supertetrahedral cationic framework with large open channels and pores. This structure allows fast anionic exchange of MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$. The most important particularity of NDTB-1 is that it exchanges TcO_4^-. The results are very promising as NDTB-1 removed 72% of Tc from solution in 36 hours. Many of synthesized uranyl borates are non-centrosymmetric and demonstrated non-linear optical properties. Our results have demonstrated that oxoborates can easily react with actinides under formation of crystalline products. Unfortunately, within the glass-blocks containing radioactive wastes potential crystallization would mechanically weaken the glass matrix and make it susceptible to possible leaching by water and ensuing release of dangerous species in the environment. Thus, it seems that our results may initiate reconsideration of the whole vitrification process of radioactive waste

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Topological aspects of Cu^{2+}—O networks.

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About 750 minerals (and much more synthetic compounds) contain Cu atoms; roughly half of them are divalent Cu^{2+} ions coordinated by any ligand *L* like oxygen and/or halogenide atoms. Despite these impressing figures only very few structure types are known exhibiting a substitution of the Cu^{2+} atoms by other cations; $Cu^{2+}L_6$ coordination figures are well known being extremely strong distorted due to the Jahn-Teller effect. The distortion of the $Cu^{2+}L_6$ polyhedron is stronger as compared to most other ions where the effect is predicted. As a consequence, the coordination figure is better described as tetragonal bipyramidal [4+2] or even tetragonal pyramidal [4+1] or square planar [4] rather than (distorted) octahedral. This is supported by common bond-valence calculations, experimentally determined parameters are given *e.g.* by [1]. The four short Cu^{2+}—O bond lengths scatter roughly around 1.97 Å going along with bond strengths ν of 0.48 valence units (*v.u.*). Consequently, more than 90 % of the formal charge of the Cu^{2+} atom is balanced by its four nearest ligands. Additional oxygen ligands are usually in a distance above 2.30 Å (0.19 *v.u.*); only a few exceptions are known. The arrangement of the additional ligands is a consequence of the O—O repulsion, space requirement of the Cu^{2+} ion, and the connection to other cations. The upper limit is not always clear. A Cu—O distance of 2.60 Å (0.08 *v.u.*) reduces the contribution to the charge balance of the Cu^{2+} atom to 4 % only and should be responsible for a very weak bond with predominantly electrostatic interactions.

There is no doubt that for compounds containing Cu^{2+} cations the topological comparison of the connection of CuO_6 polyhedra gives some insight in the structure type. However, structural details are controlled by the orientation of short and long Cu—O bonds. This is shown by a comparison of compounds related to the structure type of brucite, $Mg(OH)_2$, where layers are formed by $M^{2+}O_6$ octahedra sharing each six edges. They can be described as two sheets of O atoms forming a close-packed arrangement with the octahedrally co-ordinated positions occupied by cations. The layers are interconnected by hydrogen bonds. In compounds where the *M* sites are substituted by Cu^{2+} atoms, the orientation of the short and long Cu—O bonds modify this parental structure by moderate shifts of the O atoms. Vacant *M* sites occur frequently. Instead, the layers are decorated by (protonated) anion groups; their connection is controlled by the orientation of the axes of the tetragonal bipyramids $Cu^{[4+2]}O_6$. In $KCu_3(OH)_2[(AsO_4)H(AsO_4)]$ one of the Cu^{2+} atoms is in a very rare [2+4] coordination which obviously is stabilized by the close-packed oxygen sheets [2].

The bond-valence parameters available form literature and commonly used (e.g. [1]) are sometimes misleading for Cu^{2+} atoms. In some $Cu^{2+[4+1]}L_5$ and $Cu^{2+[4+2]}L_6$ polyhedra with exceptional short additional Cu—O distances as well as in the rare trigonal bipyramidal [5] coordination the Cu^{2+} atom often is formally over-bonded. As for many other cations, the simplified formula $ν_{ij} = \exp{[(R_{ij}\text{-}d_{ij})/0.37]}$ does not describe the bonding character for Cu^{2+} cations always sufficiently.

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