Structural richness of Cr$^{6+}$ and Cr$^{5+}$ oxysalt materials: new insights and trends

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A large amount of structural and chemical data has been accumulated recently on uranium minerals and compounds due to their high importance for nuclear waste management and understanding secondary processes of alteration of spent nuclear fuel (SNF). Uranyl chromates are of special interest, since potassium chromate solution is used as both coolant and corrosion inhibitor for some SNF rod arrays made from Mg-Be alloys. In addition, uranyl chromates are less studied than other uranyl oxysalts, due to the tendency of Cr$^{6+}$ to reduction in high-temperature hydrothermal environment. General trends in the structural chemistry of known uranyl chromates till the recent time were the same as for other uranyl oxysalts containing tetrahedral anions formed by hexavalent elements. In their structures, uranyl ions form UO$_2^-$ pentagonal bipyramids that share common vertices with CrO$_4^{2-}$ tetrahedral oxoanions in a monodentate fashion to form extended polymerized structures [1, 2, 3]. It is of interest that, in the row S$^{6+}$-Cr$^{6+}$-Se$^{6+}$-Mo$^{6+}$, structural chemistry of uranyl oxysalts with [TO$_4^{2-}$]$_2$ tetrahedral oxoanions varies significantly and there are specific trends of differences and similarities between observed structure topologies. The first examples of uranyl chromates with bidentate coordination mode have recently been reported [4,5]. In order to investigate general effects of bidentate coordination upon structural geometrical parameters in uranyl compounds, we have analysed available literature data on uranyl phosphates, arsenates, vanadates, silicates, sulfates and chromates. The results of this analysis will be discussed.

There is only one known uranyl chromate containing pentavalent Cr known to date [6]. Cr(V) is much less common in natural and technological environments than Cr(VI). Recently we have revealed that Cs(UO$_2$)$_2$Cr$^{5+}$O$_8$ occurs as a product of thermal decomposition of novel uranyl chromate Cs$_2$(UO$_2$)$_2$(Cr$^{5+}$O$_2$)$_2$ at 380°C and is stable till 620°C, which is much higher than expected previously in [6]. There are very few examples in inorganic chemistry of compounds containing both Cr$^{5+}$ and Cr$^{6+}$ cations. The combination of Cr(V) square pyramids and Cr(VI) tetrahedra creates a novel structural unit in isopropylammonium templated hydrous uranyl chromate (C$_3$NH$_{10}$)$_2$(UO$_2$)$_2$(Cr$^{5+}$O$_2$)$_2$ (Cr$^{6+}$O$_8$)(H$_2$O)$_2$(H$_2$O)$_8$ with the unprecedented complex structural topology (Fig. 1). Thus hexavalent uranium may stabilize chromium(V) in different environments. The possible reasons for such crystal chemical behaviour will be also discussed.

Keywords: uranyl oxysalts; chromates; pentavalent chromium

Fig. 1 General projection of the crystal structure of (C$_3$NH$_{10}$)$_2$(UO$_2$)$_2$(Cr$^{5+}$O$_2$)$_2$(Cr$^{6+}$O$_8$)(H$_2$O)$_2$(H$_2$O)$_8$ (a). The complex layers are formed by [(UO$_2$)$_2$(Cr$^{5+}$O$_2$)(Cr$^{6+}$O$_8$)(H$_2$O)$_2$]$_{10}$ domes (b).