

ABSTRACT

Syntheses and structural characterization of the compounds α - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, β - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$, β - $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{K}_5\text{Ce}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$, $\text{K}_2\text{Ce}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, $\text{K}_5\text{Na}[\text{Ce}_2(\text{SO}_4)_6]$, $\text{K}_6[\text{Ce}(\text{HSO}_4)_2(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$, $\text{CrCe}(\text{III})_7\text{Ce}(\text{IV})_6(\text{HSO}_4)_6(\text{SO}_4)_{21} \cdot 78\text{H}_2\text{O}$, $\text{A}_2[\text{CrCl}_5(\text{H}_2\text{O})]$, ($\text{A} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$), $\text{NH}_4\text{Cr}(\text{CrO}_4)_2$, K_2CrSO_7 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ are presented. The crystal structures have been determined from single crystal X-ray data and the thermal behavior of the hydrated binary cerium sulfates have in addition been studied by thermo-gravimetry, differential scanning calorimetry and X-ray powder thermodiffraction, *in situ* and *ex situ*. The decomposition of $\text{Ce}(\text{SO}_4)_2$, into the final product CeO_2 , proceeds through intermediate $x\text{CeO}_2 \cdot y\text{Ce}(\text{SO}_4)_2$ species. However, during the oxidative decomposition of $\text{Ce}_2(\text{SO}_4)_3$ into CeO_2 , small amount of $\text{CeO}(\text{SO}_4)$ is produced.

The four salts of the catalytically active $[\text{CrCl}_5(\text{H}_2\text{O})]^{2-}$ complex are prepared by different methods and corresponding reaction pathways are suggested. The structures of these compounds are composed of $[\text{CrCl}_5(\text{H}_2\text{O})]^{2-}$ units connected by O-H...Cl hydrogen bonds and a counter ion framework. Further, for the first time, a mixed-valence chromium oxide has been synthesized starting from CrO_3 in water solution. The reduction of the Cr(VI) into Cr(III) is presumably promoted by the oxidation of Ce(III). Among the mixed-valence chromates, $\text{NH}_4\text{Cr}(\text{CrO}_4)_2$ constitutes a new structure type forming channels, which contain the ammonium ions. Reported here is also the first crystal structure of a compound containing the CrSO_7^{2-} anion. In addition, quick high yield synthesis methods to produce $\text{Ce}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ce}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$, powerful oxidation agents, are presented.

The first rare-earth sulfate containing more than one alkali element whose structure has been described is $\text{K}_5\text{Na}[\text{Ce}_2(\text{SO}_4)_6]$. Its structure consists of pairs of edge sharing cerium polyhedra, interlinked by edge and corner sharing sulfate groups, forming layers connected by potassium ions. Also the acidic $\text{K}_6[\text{Ce}(\text{HSO}_4)_2(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$ differs from previously known rare-earth sulfates. It is unique and constitutes a new structure type since it contains rare-earth monomers, $[\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^{5-}$.

The existence of alterable oxidation states for the cerium ion has resulted in crystals of two mixed-valence cerium sulfates. In the structure of $\text{K}_5\text{Ce}_2(\text{SO}_4)_6 \cdot \text{H}_2\text{O}$, there are pairs of edge sharing cerium polyhedra with one delocalized f^1 electron. The cerium polyhedra are linked through edge and corner sharing sulfate bridges thereby forming layers joined by potassium ions. The oxidation state of each cerium ion is a mean value between III and IV, which may contribute to new unique properties. The structure of $\text{CrCe}(\text{III})_7\text{Ce}(\text{IV})_6(\text{HSO}_4)_6(\text{SO}_4)_{21} \cdot 78\text{H}_2\text{O}$ differs significantly from previously known structures of mixed-valence cerium compounds. It extends to form layers through which there are large open channels, c.a. 10 Å diameter. A mixed-valence compound with this type of structural architecture may be a base for new attractive applications in the future.

Keywords: Mixed-valence; Oxidizing agents; Cerium sulfates; Cerium chromates; Aquapentachlorochromate(III); Redox reactions; X-ray diffraction; Thermal behavior.