

Fehlende Glieder bekannter Reihen:

Die Oxoferate(III) $\text{Rb}_8[\text{Fe}_2\text{O}_7]$, $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ und $\text{K}_4[\text{Fe}_2\text{O}_5]$

Missing Links in Known Series: The Oxoferates(III) $\text{Rb}_8[\text{Fe}_2\text{O}_7]$, $\text{Rb}_6[\text{Fe}_2\text{O}_6]$, and $\text{K}_4[\text{Fe}_2\text{O}_5]$

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The title compounds were synthesized at temperatures between 775 and 1175 K from (mostly stoichiometric) mixtures of Fe_2O_3 , elemental rubidium or potassium (A) and their hyperoxides AO_2 . The structures have been determined by single crystal X-ray diffraction. The alkaline rich ferrate(III) $\text{Rb}_8[\text{Fe}_2\text{O}_7]$ ($\text{Cs}_8[\text{Fe}_2\text{O}_7]$ structure type, space group $P2_1/c$, $a = 696.7$, $b = 1722.1$, $c = 692.0$ pm, $\beta = 119.40^\circ$, $Z = 2$, $R1 = 0.0496$) exhibits diferrate anions $[\text{Fe}_2\text{O}_7]^{8-}$ composed of two vertex-sharing $[\text{Fe}^{\text{III}}\text{O}_4]$ tetrahedra with a linear Fe-O-Fe bridge and nearly ideal $3m$ symmetry. This is in marked contrast to the Na homologue, where the diferrate anions are decidedly angular. In the series $\text{A}_3[\text{FeO}_3]$, the anions in the compounds of the light alkaline cations are chains ${}^\infty[\text{FeO}_2\text{O}_{2/2}]^{3-}$, but similar to the isotypic $\text{K}_6[\text{Fe}_2\text{O}_6]$ and to $\text{Cs}_6[\text{Fe}_2\text{O}_6]$ the new ferrate $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ ($\text{K}_6\text{Fe}_2\text{O}_6$ structure type, space group $C2/m$, $a = 741.8(2)$, $b = 1148.7(2)$, $c = 680.08(12)$ pm, $\beta = 103.65(2)^\circ$, $Z = 4$, $R1 = 0.0370$) contains isolated binuclear anions $[\text{O}_2\text{FeO}_2\text{FeO}_2]^{6-}$ composed of two edge sharing $[\text{FeO}_4]$ tetrahedra. The new potassium ferrate of the series $\text{A}_4[\text{Fe}_2\text{O}_5]$, $\text{K}_4[\text{Fe}_2\text{O}_5]$ (space group $P2_1/c$, $a = 645.91(14)$, $b = 593.69(13)$, $c = 1003.0(2)$ pm, $\beta = 103.124(4)^\circ$, $Z = 4$, $R1 = 0.0355$), constitutes a new structure type, but its structure is still closely related to the Na compound, which crystallizes in the isomorphous subgroup $P2_1/n$ with a doubled a axis. Both compounds are phylloferrates with layers ${}^\infty[\text{Fe}_2\text{O}_5]^{4-}$ consisting of six-membered rings of $[\text{FeO}_4]$ tetrahedra. In contrast, $\text{Rb}_4[\text{Fe}_2\text{O}_5]$ contains chains of vertex and edge sharing tetrahedra, so that in both series, $\text{A}_3[\text{FeO}_3]$ and $\text{A}_4[\text{Fe}_2\text{O}_5]$, the linkedness of the ferrate tetrahedra increases with the ionic radii of the A counterions.

Key words: Ferrates, Rubidium, Potassium