Lanthanoidhaltige Komplexe monovakanter Keggin- und Dawson-Polyoxoanionen

Novel Lanthanide Complexes of Monovacant Keggin- and Dawson-Type Polyoxoanions

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The new polyoxotungstates $Cs_{6n}K_{2n}[\{(Pr(H_2O)_7)(Pr(H_2O)_2)(\alpha\text{-}SiW_{11}O_{39})\}_4]_n \cdot 33nH_2O$ (**1**), $(NH_4)_{14}[\{Tb(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2] \cdot 39H_2O$ (**2**) and $(NH_4)_{7.33}K_{2.67}Ho_{1.33}[\{Ho(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2] \cdot 45H_2O$ (**3**) were synthesized in aqueous solution and characterized by IR and Raman spectroscopy, ^{31}P NMR spectroscopy (for **2** and **3**), energy dispersive X-ray fluorescence analysis and single-crystal X-ray analysis. **1** exhibits a novel one-dimensional chain-like structure which is built up from of monovacant $(\alpha\text{-}SiW_{11}O_{39})^{8-}$ Keggin-type anions linked by Pr(III) atoms. Half of the Pr(III) atoms are eight-coordinate (square antiprism), with four sites occupied by one anion, three by water molecules, and the eighth site by a terminal oxygen atom of a second anion. The other Pr(III) atoms are coordinated by seven water molecules and two terminal oxygen atoms of two Keggin moieties. The dimeric $[\{Ln(H_2O)_3(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ anions in **2** (Ln = Tb) and **3** (Ln = Ho) consist of two $(\alpha_2\text{-}P_2W_{17}O_{61})^{10-}$ Dawson-type anions linked by two trivalent lanthanides. The lanthanides exhibit a square-antiprismatic coordination sphere which is built up by three water molecules, four terminal oxygen atoms of one Dawson-anion and one oxygen atom of the second Dawson-anion. The crystal structures of the new compounds are compared with known species and the influence of the Ln(III) ionic radii is discussed.

Key words: Lanthanides, Polyoxometalates, Self-Assembly, Tungsten