Dodekahydro-*closo*-Dodekaborat-Halogenide der schweren Alkalimetalle mit der Formel $M_3X[B_{12}H_{12}]$ (M = K – Cs, NH_4; X = Cl und Br)

Dodecahydro-*closo*-dodecaborate Halides of the Heavy Alkali Metals with the Formula $M_3X[B_{12}H_{12}]$ (M = K – Cs, NH_4; X = Cl and Br)

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The solvent-free dodecahydro-*closo*-dodecaborate chlorides $M_3Cl[B_{12}H_{12}]$ ($M^+ = Rb^+, Cs^+$) and bromides $M_3Br[B_{12}H_{12}]$ ($M = K^+ - Cs^+, NH_4^+$) of the heavy alkali metals are easily accessible by recrystallization of the corresponding $M_2[B_{12}H_{12}]$ salts from aqueous solutions of the respective alkali-metal chlorides (MCl) or bromides (MBr). After precipitation colourless, polyhedral-shaped single crystals were obtained and characterized by X-ray diffraction at room temperature. The compounds are all isostructural and crystallize in the trigonal space group *R*3*m* with $Z = 3$ ($Rb_3Cl[B_{12}H_{12}]$: $a = 1009.73(7)$, $c = 1139.14(9)$ pm; $Cs_3Cl[B_{12}H_{12}]$: $a = 1038.02(7)$, $c = 1179.59(9)$ pm; $K_3Br[B_{12}H_{12}]$: $a = 1002.34(7)$, $c = 1117.68(9)$ pm; $(NH_4)_3Br[B_{12}H_{12}]$: $a = 1015.61(7)$, $c = 1138.70(9)$ pm; $Rb_3Br[B_{12}H_{12}]$: $a = 1016.89(7)$, $c = 1141.82(9)$ pm; $Cs_3Br[B_{12}H_{12}]$: $a = 1045.53(7)$, $c = 1185.47(9)$ pm). Their structures are best described as a trigonally distorted variant of an *anti*-perowskite arrangement, the *anti*-$LaAlO_3$-type structure. Together, the *quasi*-icosahedral $[B_{12}H_{12}]^{2-}$ cluster anions and the M^+ cations build up a cubic close-packed host structure where the halide anions (X^-) occupy all those octahedral interstices which are exclusively formed by the cations. The thermal decomposition of the salts was investigated by thermal analysis with DTA/TG methods in the temperature range between 30 and 1200 °C. The solid salts were also characterized using IR and Raman spectroscopy. The observed splitting of the B−H and B−B absorption bands clearly indicates a loss of symmetry of the *quasi*-icosahedral dianionic $[B_{12}H_{12}]^{2-}$ clusters.

Key words: Alkali Metal Salts, Dodecahydro-*closo*-dodecaborates, Halides, Thermal Analysis (DTA/TG), IR and Raman Spectroscopy