Dodekahydro-closo-Dodekaborat-Halogenide der schweren Alkali-
metalle mit der Formel $M_3 X[B_{12}H_{12}]$ (M = K – Cs, NH$_4$; X = Cl und Br)

Dodecahydro-closo-dodecaborate Halides of the Heavy Alkali Metals with the Formula $M_3 X[B_{12}H_{12}]$ (M = K – Cs, NH$_4$; X = Cl and Br)

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The solvent-free dodecahydro-closo-dodecaborate chlorides $M_3 Cl[B_{12}H_{12}]$ ($M^+ = $ Rb$^+$, Cs$^+$) and bromides $M_3 Br[B_{12}H_{12}]$ ($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 $R\bar{3}m$ with $Z = 3$ (Rb$_3$Cl$[B_{12}H_{12}]$: $a = 1009.73(7)$, $c = 1139.14(9)$ pm; Cs$_3$Cl$[B_{12}H_{12}]$: $a = 1038.02(7)$, $c = 1179.59(9)$ pm; K$_3$Br$[B_{12}H_{12}]$: $a = 1002.34(7)$, $c = 1117.68(9)$ pm; (NH$_4$)$_3$Br$[B_{12}H_{12}]$: $a = 1015.61(7)$, $c = 1138.70(9)$ pm; Rb$_3$Br$[B_{12}H_{12}]$: $a = 1016.89(7)$, $c = 1141.82(9)$ pm; Cs$_3$Br$[B_{12}H_{12}]$: $a = 1045.53(7)$, $c = 1185.47(9)$ 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, Dodekahydro-closo-dodecaborates, Halides, Thermal Analysis (DTA/TG), IR and Raman Spectroscopy