

# Formamidinium Salts of Low Valent Metal Halide Anions $\text{MX}_3^-$ ( $\text{M} = \text{Ge}, \text{Sn}$ ) and $\text{M}_2\text{X}_6^{2-}$ ( $\text{M} = \text{Ga}, \text{In}$ )

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 70<sup>th</sup> birthday*

Tetramethylformamidinium trichlorogermanite,  $[\text{CH}(\text{NMe}_2)_2][\text{GeCl}_3]$ , tetramethylformamidinium trichlorostannite,  $[\text{CH}(\text{NMe}_2)_2][\text{SnCl}_3]$ , *bis*-(tetramethylformamidinium hexaiododigallate,  $[\text{CH}(\text{NMe}_2)_2]_2[\text{Ga}_2\text{I}_6]$  and *bis*-(tetramethylformamidinium hexachlorodiindate,  $[\text{CH}(\text{NMe}_2)_2]_2[\text{In}_2\text{Cl}_6]$  have been prepared by the reactions between tetramethylformamidinium chloride,  $[\text{CH}(\text{NMe}_2)_2]\text{Cl}$ , and the corresponding low valent halides  $\text{GeCl}_2$  (as dioxane adduct),  $\text{SnCl}_2$ , “GaI” and  $\text{InCl}$ . Their crystal structures have been determined by single crystal X-ray diffraction.  $[\text{CH}(\text{NMe}_2)_2][\text{GeCl}_3]$  aggregates in a centrosymmetric dimeric structure, in which two trigonal pyramidal  $\text{GeCl}_3$  units are connected together by two weak  $\text{Ge}\cdots\text{Cl}$  bonds and each Ge atom is bonded to one cation by a weak  $\text{Ge}\cdots\text{N}$  contact. Two sets of weak hydrogen bonds  $\text{C-H}\cdots\text{Cl}$  are observed with bond lengths of 2.87(2) Å and 2.85(2) Å. In  $[\text{CH}(\text{NMe}_2)_2][\text{SnCl}_3]$ , the  $\text{SnCl}_3^-$  units adopts a (3+3) coordination with three normal Sn-Cl bonds and three weak  $\text{Sn}\cdots\text{Cl}$  contacts.  $[\text{CH}(\text{NMe}_2)_2]_2[\text{Ga}_2\text{I}_6]$  and  $[\text{CH}(\text{NMe}_2)_2]_2[\text{In}_2\text{Cl}_6]$  contain metal-metal bonded anions with distorted staggered ethane-like conformations. The metal-metal bond lengths are 2.423(1) Å (Ga-Ga) and 2.719(1) Å (In-In). Their Raman spectra contain intense bands at 118.7  $\text{cm}^{-1}$  (Ga-Ga) and 174.7  $\text{cm}^{-1}$  (In-In) associated with metal-metal stretching modes.

*Key words:* Formamidinium Salts, Germanite, Stannite, Digallate, Diindate