Crystal Structures and Thermal Behavior of Isostructural Bis(dibenzyldimethylammonium) Tetrachlorometallate [*M* = Mn(II), Co(II), Ni(II) and Zn(II)] Solvates Crystallized from Acetonitrile and/or Methanol Solutions

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Five isostructural bis(dibenzyldimethylammonium) tetrachlorometallate solvate complexes [*M* = Mn(II), Co(II), Ni(II) or Zn(II)] were crystallized from acetonitrile and/or methanol solutions. The crystal structures are compared to those of the analogous, isostructural copper compounds (*X* = Cl or Br) reported earlier. The complexes crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$, and unit cell dimensions of $a \approx 14.1$, $b \approx 16.1$, $c \approx 15.7$ Å and $\beta \approx 108 - 109°$. The asymmetric unit of these compounds contains one MCl_4^{2-} anion, two $Bz_2Me_2N^+$ cations in the W-conformation and one half of a disordered solvent molecule (acetonitrile or methanol). The geometry of the MCl_4^{2-} anion is close to tetrahedral, whereas the analogous copper anions appeared in distorted tetrahedral geometries with *trans* angles of 124.4° for *X* = Cl and 123.6° for *X* = Br. In addition to the ionic interactions between the cations and the anions, the components are connected by weak C–H···Cl$^-$ bonds. As a distinction between the two crystallographically independent cations in the asymmetric unit, one type of independent cations form long chains *via* weak edge to face π–π interactions along the crystallographic *b* axis, whereas the other type of cations are not tied together by such weak π–π interactions. The coordination around the N atoms is also nearly tetrahedral, and neither static nor dynamic disorder of the $Bz_2Me_2N^+$ cations can be observed. The complexes are thermally stable and melt close to the decomposition temperatures in the range 170 – 205 °C.

Key words: Quaternary Ammonium Compound, Tetrachlorometallate, Tetrahalometallate, X-Ray Single Crystal Diffraction, Thermal Studies