

Crystal Structures and Thermal Behavior of Bis(dibenzyltrimethylammonium) Tetrabromometallates(II) [$M = \text{Mn(II)}$, Co(II) and Zn(II)] and Their Solvates

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Six new A_2MBr_4 structures [$A = \text{dibenzyltrimethylammonium cation}$, $M = \text{Mn(II)}$, Co(II) or Zn(II)] were crystallized with or without solvent molecules from acetonitrile, methanol and/or aqueous solutions. The isomorphous compounds $[(Bz_2Me_2N)_2][MnBr_4] \cdot CH_3CN \cdot H_2O$ (**1**) and $[(Bz_2Me_2N)_2][ZnBr_4] \cdot CH_3CN \cdot H_2O$ (**4**) crystallize in the triclinic space group $P\bar{1}$ from acetonitrile solutions. The solvent molecules participate in the hydrogen bonding network inside the crystal structure. $[(Bz_2Me_2N)_2][CoBr_4] \cdot 0.5CH_3CN$ (**2**) crystallizes from an acetonitrile solution in the monoclinic space group $P2_1/c$. The solvent molecules fill the voids of the crystal structure. Compound **2** is isostructural with the previously reported compounds $[(Bz_2Me_2N)_2][MCl_4] \cdot 0.5CH_3CN$ with $M = \text{Mn(II)}$, Co(II) , Ni(II) , Cu(II) or Zn(II) . $[(Bz_2Me_2N)_2][CoBr_4]$ (**3**) and $[(Bz_2Me_2N)_2][ZnBr_4]$ (**5a**) crystallize from a methanol solution in the monoclinic space group $P2_1/c$ without solvents. A polymorph of compound **5a**, $[(Bz_2Me_2N)_2][ZnBr_4]$ (**5b**), was crystallized from aqueous solution in the monoclinic space group $P2_1/c$. The packing of the components of the two polymorphs differs clearly. One cation of **5a** appears in the W-conformation whereas the other cation of **5a** and both cations of **5b** appear in twisted conformations. In addition to the ionic interactions between the ion pairs, the packing of the compounds is stabilized by hydrogen bonds and weak intermolecular $\pi-\pi$ interactions in all cases. The compounds melt around 200 °C and decompose mainly in two steps just above the melting point. Slow evaporation of solvents is observed both in the TG and DSC diagrams of the solvates (**1**, **2** and **4**) below 100 °C.

Key words: Quaternary Ammonium Compound, Tetrabromometallate, Tetrahalometallate,
X-Ray Single Crystal Diffraction, Thermal Analysis