

Synthesis and single crystal structure determination of a new mixed-metal organic–inorganic hybrid of discrete transition metal halide complexes and α , ω -diammonioalkane assembled through non-covalent intermolecular interactions: $[\text{NH}_3(\text{CH}_2)_6\text{NH}_3]_4[\text{RhCl}_6][\text{FeCl}_4]\text{Cl}_4$

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In this work, we report a single-crystal structure of a new organic-inorganic hybrid material based on two different mononuclear halogenidometallate complexes, in which hexachloridorhodate (III) ($[\text{RhCl}_6]^{3-}$), tetrachloridoferrate (III) ($[\text{FeCl}_4]^-$) and chloride ions (Cl^-) are combined with the organic cation 1,6-diammoniumhexane ($\text{C}_6\text{H}_{18}\text{N}_2^{2+}$) to form a three-dimensional (3D) framework *via* non-covalent ‘intermolecular’ interactions. Tetrakis(1,6-diammoniumhexane) hexachloridorhodate(III) tetrachloridoferrate(III) tetrachloride has been hydrothermally synthesized in concentrated hydrochloric acid solution. Red single crystals of the compound with sufficient size for X-ray structure determination were grown by slow evaporation of the hydrochloric acid solution of the hydrothermally treated reactants. The crystal structure analysis indicates that the titled compound crystallizes in the tetragonal space group $I4_1/a$ with unit cell dimensions $a = 19.154(3)$ Å, $c = 14.363(3)$ Å, and $Z = 4$. The solid with the sum formula $\text{C}_{24}\text{H}_{72}\text{Cl}_{14}\text{FeN}_8\text{Rh}$ is formed by three types of distinct anionic units, $[\text{RhCl}_6]^{3-}$, $[\text{FeCl}_4]^-$ and Cl^- , which are charge balanced by cations $[\text{C}_6\text{H}_{18}\text{N}_2]^{2+}$. The asymmetric unit consists of one Rh, one Fe and one chloride atom *viz.* atom Cl(4), on special positions (fourfold axes, glide plane), three chloride atoms *viz.* atom Cl(3), Cl(2) and Cl(1), and one complete all-transoid zigzag chain-like 1,6-diammoniumhexane dication is placed in general positions. Cl(4) and Cl(3) occupy the axial and equatorial positions, respectively, in the slightly distorted octahedral geometry around Rh with bond lengths $\text{Rh}-\text{Cl}(4) = 2.344(3)$ Å and $\text{Rh}-\text{Cl}(3) = 2.355(2)$ Å. Cl(2) fills the coordination sphere in the tetrahedral geometry around Fe with bond length $\text{Fe}-\text{Cl}(2) = 2.166(4)$ Å. Figure 1 depicts the asymmetric unit with atom numbering and colour legend. $[\text{C}_6\text{H}_{18}\text{N}_2]_4[\text{RhCl}_6][\text{FeCl}_4]\text{Cl}_4$ is isomorphous with the organic-inorganic hybrid compound containing 1,6-diammoniumhexane, hexachloroferrate (III), tetrachloroferrate (III) and chloride ions $[\text{C}_6\text{H}_{18}\text{N}_2]_4[\text{FeCl}_6][\text{FeCl}_4]\text{Cl}_4$ [1,2]. The solid-state structure of $[\text{C}_6\text{H}_{18}\text{N}_2]_4[\text{RhCl}_6][\text{FeCl}_4]\text{Cl}_4$ features a three-dimensional network of $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds between the ionic components. The $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds donate from the protonated amino groups (NH_3^+) at both ends of the organic ion to the chloride ligands of $[\text{RhCl}_6]^{3-}$ and free chloride ions with $\text{NH}\cdots\text{Cl}$ distances ranging from 3.124(8) to 3.309(7) and are to be considered as weak interactions. Inorganic layers are built up from $[\text{RhCl}_6]^{3-}$ octahedral and $[\text{FeCl}_4]^-$ tetrahedral which are arranged in line along the crystallographic *c*-axis and the distance between metal centers is long (7.181 Å); the organic cationic species along with the free chloride anions are located between the inorganic layers and bound to each other by further $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds. In contrast, $[\text{FeCl}_4]^-$ does not participate in any hydrogen bonding of significant strengths. It seems, the free chloride and $[\text{RhCl}_6]^{3-}$ ions have priority to interacting with $[\text{C}_6\text{H}_{18}\text{N}_2]^{2+}$. The titled organic-inorganic hybrid compound was also characterized by Fourier-transform infrared spectroscopy (FT-IR), elemental and differential scanning calorimetry (DSC) analyses, and powder X-ray diffraction (XRD). To the best of our knowledge, it is the example of a mixed-metal organic-inorganic hybrid compound based on mononuclear transition metal halide complexes.

Keywords: Organic-inorganic hybrid compound, rhodium (III) halide; iron (III) halide; α , ω -diammonioalkane, crystal engineering; non-covalent intermolecular interactions