Thiolate halide copper(I) 2D coordination polymers with thermochromic luminescent properties

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Compounds \([\text{Cu}_3\text{X(HT)}_2]_n\) and \([\text{Cu}_3\text{Br(HT)}_2]_n\) are isostructural. The crystal structure displays layers of 2D polymers parallel to the oc plane. In the image is shown the stacking of two layers of \([\text{Cu}_3\text{I(HT)}_2]_n\), viewed along the c axis, from the data collected at room temperature.

Coordination environments of \(\text{Cu}_1\) (left) and \(\text{Cu}_2\) (right) at 296 K, both planar trigonal.

Three new 2D polymeric copper(I) thiolates with formula \([\text{Cu}_3\text{X(HT)}_2]_n\) \((\text{X} = \text{Cl, Br, I}; \text{HT} = 4\text{-hydroxythiophenolate})\) have been synthesised by solvothermal procedures. The crystal structures of these coordination polymers have been solved by single crystal X-ray diffraction. They display a similar layered structure with the hydroxyl groups from the HT ligands joining the polymeric sheets by hydrogen bonds.

These compounds present a strong orange emission at room temperature. A reversible thermochromic effect is observed on cooling, stronger in the iodine derivative, where the emission changes colour from orange, at room temperature, to green at lower values. Photoluminescent properties have been studied at different temperatures, and the disappearance of the lower energy band is observed with decreasing temperature, together with an increase in the intensity of the more energetic band. Changes in the luminescent properties are associated with the structural modifications observed in the crystal structures solved both at 296 and at 110 K, in particular, with the shortening of \(\text{Cu}_1\)-\(\text{Cu}_3\) distances in the inorganic 2D layers.

Compound \([\text{Cu}_3\text{I(HT)}_2]_n\), although not strictly isostructural with the chlorine and bromine derivatives (as it crystallises in a different space group) displays a very similar arrangement of the polymeric layers, parallel to the \(bc\) plane in this case. In the image is shown the stacking of two layers of \([\text{Cu}_3\text{I(HT)}_2]_n\), viewed along the \(c\) axis, from the data collected at room temperature.

The asymmetric unit contains one 4-hydroxythiophenolate ligand coordinated by the sulfur atom, one half iodine atom, and one and a half crystallographically different \(\text{Cu}_1\) atoms (depicted in two different shades of blue). Both the halogen ligand and the sulfur atom act as μ₂ bridges joining two \(\text{Cu}_1\) and one \(\text{Cu}_2\) atoms.

Coordination environments of \(\text{Cu}_1\) (left) and \(\text{Cu}_2\) (right) at 110 K, with the one around \(\text{Cu}_2\) is very similar (with shorter bond distances), the one around \(\text{Cu}_1\) changes as two \(\text{Cu}_1\) join in a metal-metal bond.

View of the inorganic layer where the coordination environments of both copper atoms can be seen (left) and lateral view of this layer in the \(c\) direction, at 296 K.

The asymmetric unit contains one 4-hydroxythiophenolate ligand coordinated by the sulfur atom, one half iodine atom, and one and a half crystallographically different \(\text{Cu}_1\) atoms (depicted in two different shades of blue).

In this structural type, the sulfur atoms act as \(\mu_2\) bridges joining two \(\text{Cu}_1\) and one \(\text{Cu}_2\) atoms, while the iodine ones present a \(\mu_3\) mode bridging two \(\text{Cu}_2\) and two \(\text{Cu}_1\) atoms.

Coordination environments of \(\text{Cu}_1\) (left) and \(\text{Cu}_2\) (right) at 296 and at 110 K.

In this case the environments do not change, although most of the bond distances get shorter with low temperature.

View of the inorganic layer where the coordination environments of both copper atoms can be seen (left) and lateral view of this layer in the \(c\) direction, at 110 K.