Structural variability of dimeric copper(II) salicylate(2-) complexes

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Salicylated copper complexes exhibit interesting biological properties such as anti-convulsant, antimicrobial, superoxide dismutase mimetic, cytotoxic activities [1-4] as well as showing promising chemotherapeutic potential [3].

In the framework of the study of potenial applications in bioinorganic chemistry, several dimeric copper(II) salicylate(2-) complexes were prepared and structurally characterized. The compounds have the general formula [Cu(X-sal)(bpy)]2 where X-sal are the anions(-) of 3-chlorosalicylic (3-Clsal), 4-chlorosalicylic (4-Clsal), 4-bromosalicylic (4-Brsal), 3,5-dichlorosalicylic (3,5-Cl_2sal) and 3,5-diiodosalicylic (3,5-I_2sal) acids. All of these complexes have a dimeric molecular structure (Figure 1) but but differ in the manner of bridging the salicylate(2-) anion as a ligand. In the studied series, the modes of the salicylate(2-) anions were observed: one bridging phenolic oxygen atom, one bridge carboxyl oxygen atom, and three bridge carboxylate atoms (oxygen-carbon-oxygen atoms) (Figure 1).

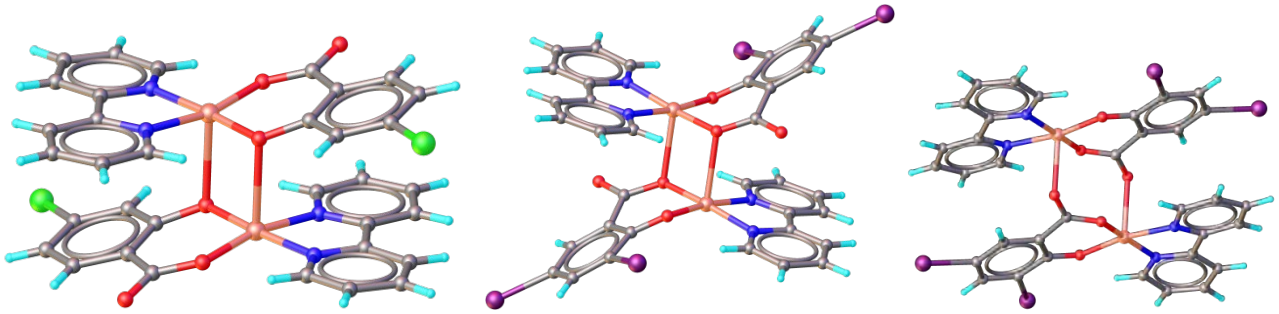

Figure 1. Molecular structure of the complex $[Cu(4\text{-}Clsal)(bpy)]_2$ and two isomers of the complex $[Cu(3,5\text{-}I_2sal)(bpy)]_2$.

The dimer complexes show further structural features of interest. The crystal structures of the two isomers of $[Cu(3,5\text{-}I_2sal)(bpy)]_2$ are examples of bond isomerism of the bridging 3,5-diiodosalicylate(-) anion. The $[Cu(4\text{-}Clsal)(bpy)]_2$ complex shows a temperature-induced phase transition, and the $[Cu(3\text{-}Clsal)(bpy)]_2$ complex exists in several pseudopolymorphs.
The crystal structure of the complex with anion(2-) of 3-bromosalicylic acid (3-Brsal) is polymeric, unlike previous dimer complexes. This polymer complex has the formula $[Cu(3\text{-}Brsal)(bpy)]_n$ and the 3-bromosalicylate(2-) anion is a three-atom bridge.

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