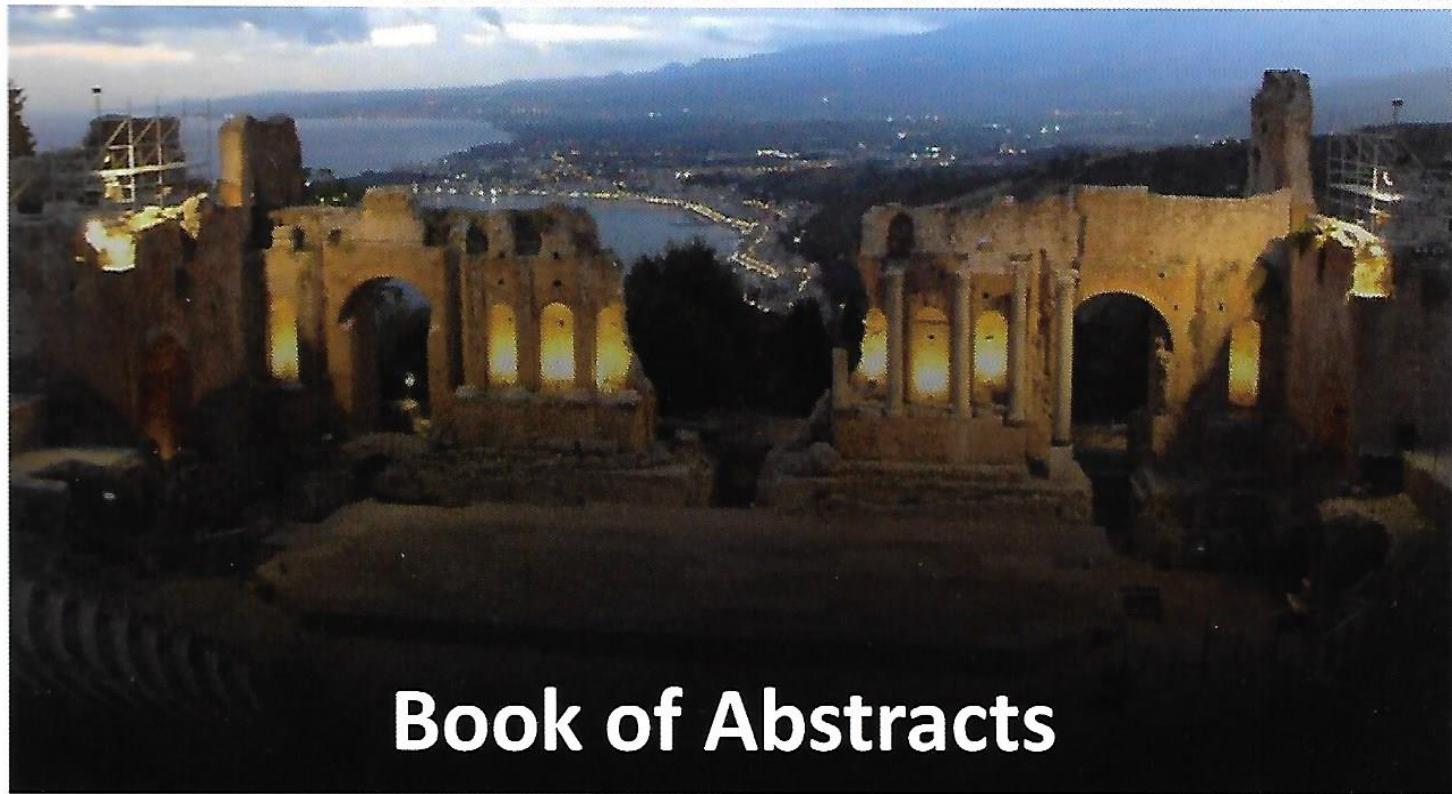




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Iodide and Triiodide Anion Complexes with a Tetrazine-Based Ligand

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Polyiodides are able to give rise to a multitude of different structures, ranging from simple discrete units to three-dimensional networks, passing from linear chains and two-dimensional arrangements. To date, the three simple building blocks I_2 , I^- and I_3^- , has been found to form polyanions as complex as I_{29}^{3-} . Such a fascinating structural diversity is the result of the ability of iodine-based species to organize themselves through donor-acceptor interactions. The theoretical interest in these systems and in the nature of the bonding within multivalent iodine-based networks is paired with a consistent practical investigation, arising from the interesting electrical properties of these species and their application as conductive polymers.

Here we report the formation of several different complexes of the tetrazine-based ligand L (Figure 1) with iodide and triiodide anions, whose structures have been determined by X-ray diffraction technique on single crystals. The ligand L was found to form two different crystal structures when dissolved in aqueous solutions of iodide. Within the first few hours after mixing H_2L^{2+} and I^- in aqueous solution, single crystals of the complex shown in Figure 2 could be isolated. Afterwards, due to a slow air oxidation of iodide to form triiodide, a new species becomes more stable, causing the dissolution of the previously formed crystals and the formation of new ones, whose crystal structure is reported in Figure 3.

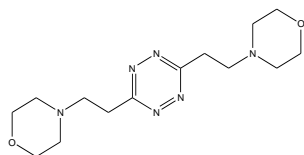


Figure 1

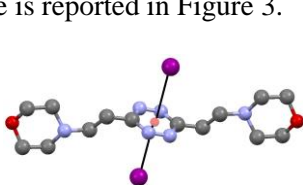


Figure 2
[H₂L(I)₂]·H₂O

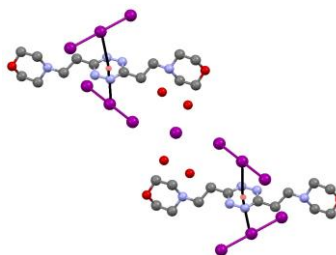


Figure 3
[(H₂L)₂I(I₃)₃]·4H₂O

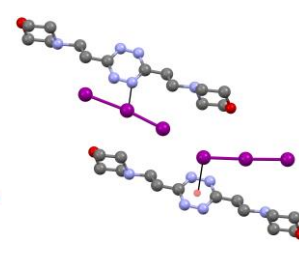


Figure 4
[H₂L(I₃)₂]·H₂O

While the first structure (Figure 2) shows the binding of the iodide anion to the heterocycle through anion- π interaction, the second one (Figure 3) shows the “side-on” binding of the triiodide anion to the ring, while the iodide anion is confined in a three-dimensional pocket defined by ligand molecules, triiodide anions and water molecules. A third type of crystals, featuring only triiodide anions, could be obtained by diffusion of a solution of triiodide into an acidic ligand solution inside an H-shaped tube. Its structure, shown in Figure 4, reveals the presence of two symmetrically non-equivalent triiodide anions organized in infinite ABAB polyiodide chains. One of them is bent ($\alpha=174^\circ$) and is located above the tetrazine ring where it interacts “side on” with a tetrazine nitrogen. The other one interacts “end-on” with the tetrazine centroid.

Further analysis of the obtained crystal samples containing the triiodide anion was performed through micro and FT-Raman techniques. Theoretical calculations to evaluate the nature of the interaction of these anions with the heterocycle will also be performed.