ISMEC 2021

International Symposium on Thermodynamics of Metal Complexes

Białystok, June 16th-18th

Acta of the International Symposia on Thermodynamics of Metal Complexes

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I S Me C

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Polyiodide complexes: the thin line between coordination chemistry and crystal engineering

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Since the discovery of iodine, two centuries ago, polyiodide chemistry has been object of intense scientific curiosity [1,2]. In its various historical iterations, the field attracted experts with diverse interests, including bonding theories (easily challenged by hypervalent polyiodides), nature of I···I supramolecular interactions (eventually leading to concepts such as secondary/σ-hole/halogen bonding), and solution thermodynamics (equilibria in I_2/I^- solutions have been long debated and their study remains experimentally challenging to these days) [1,2]. Nowadays, together with a renewed interest for novel media (ionic liquids, iodine-doped polymers, etc…), crystal engineering of polyiodides remains a lively field of study, allowing both for the prosecution of the elucidation of the basic properties of such systems and the simultaneous obtainment of crystalline phases with potential for application (especially as solid-state electrical conductors based on a Grotthuss-like mechanism) [1,2].

What we intend to discuss is the impossibility to address crystal engineering of polyiodide-based systems, or even to meaningfully obtain series of polyiodide crystals in the first place, without considering the serious, and challenging, speciation problem that arises when I_2, I^-, and cations with systematic structural changes co-exist in solution. We will show how pre-emptive knowledge of cation and anion speciation in solution is required to ensure that observed polyiodide structural changes are truly function only of intended changes in the cations, and how strict control of crystallization conditions (accounting for solution equilibria) must be maintained to establish meaningful structure-properties relationships.

As incorporation of transition metals in iodine-dense polyiodide networks is of potential technological interest, we will focus on solution thermodynamics and coordination chemistry as necessary tools of the trade for the engineering of such crystalline phases.

References:

[1] P. H. Svensson, L. Kloo, *Chem. Rev.* **2003**, 103(5), 1649-1684.
[2] M. Savastano, *Dalton Trans.* **2021**, 50, 1142-1165.