

MS36 Structure and function in inorganic and coordination complexes

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Selection of tautomers in the solid state driven by metals and other inorganic components

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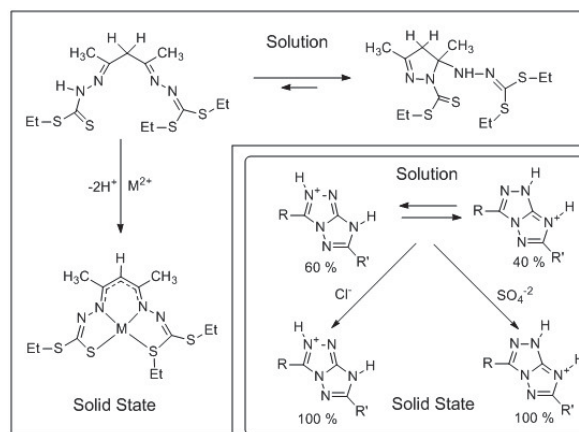
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Tautomers are structural isomers in ready equilibrium between each other. In the most common case of tautomerism, i. e. prototropism, tautomers differ for the position of hydrogen atoms inside the molecule and for the distribution of π electrons.

In a certain sense, tautomers can be considered as "living molecules", because of the thermodynamic equilibrium they undergo. In fact, the relative amounts of the forms can be altered by physical or chemical factors (temperature, solvent, pH, mechanochemical processes etc.), and so a tautomeric system can face a change in ambient conditions by favouring one form over the others. This responsiveness of tautomeric systems is appealing for the development of smart materials.

The dynamic equilibrium between the different tautomeric forms of a compound in solution can lead to different outcomes for the crystallization from solution: crystallization of only one tautomeric form (likely, but not necessarily, the most stable in solution), co-crystallization of different tautomers in the same lattice, concomitant formation of crystals of different tautomeric forms. Altogether, crystallization of different tautomers of the same compound is a rare occurrence and only around 0.5 % of molecules able to tautomerize and archived in the Cambridge Structural Database are actually observed in different tautomeric forms in the solid state.¹ This can be related with the fact that for many potentially tautomeric systems, the energy difference between the tautomers is high (>3 kcal/mol) and so only one form is prevailing by far in solution and found in the crystals.

In the present communication, we will discuss examples of tautomeric systems for which, out of many tautomers present in solution, the selective precipitation of only one tautomer is achieved in the solid state. The selectivity is provided by metal complexation² or by formation of salts with suitable inorganic counterions.³ Examples include ring to open-chain tautomerization in dithiocarbazate ligands and tautomers of neutral and singly protonated N-rich fused-ring triazolotriazoles.



References:

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