Two different types of supramolecular architectures of p-sulphonated thiacalix[4]arene with Zn(bipy)$_2$$^{2+}$: Structure and stability.

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Sulphonated calix[n]arenes are of great interest as objects of supramolecular chemistry due to their multi-functional complexation abilities and a variety of the conformational forms.

Previously in [1] we reported the structure of the thiacalix[4]arene tetrasulphonate (TCAS) complex 1 with [Zn(bipy)$_2$]$^{2+}$ and water. TCAS didn’t participate in coordination bonding with metal and possessed a partial cone conformation. At the same time NMR measurements of the solution showed that 1,2-alternate-TCAS may be bound with the dichelated forms of [Zn(bipy)$_2$]$_n$ ($n = 1, 2$) in its bi- or tridentate coordination sites.

Crystals 2 of different colour and habit were found together with crystals 1 in the same flask. But they appeared to be twinned and unstable when exposed to air and so required more gentle treatment.

Recent X-ray diffraction analysis of single crystal 2 has revealed a new type of mixed ligand complex (see picture below). This complex is one of those ($n = 1$) predicted by NMR studies of the mother solution. It co-crystallizes with two [Zn(bipy)$_2$]$_2$$^{2+}$ per thiacalixarene macrocycle and with disordered solvent. Obviously the evaporation of the solvent from crystal is the cause of its instability.

Time-resolved X-ray powder diffraction experiment of powder 2 was carried out to analyze its decomposition. It has been proved that the decomposition product 3 is crystalline but differs from 1 and 2. The details of the structural changes during crystal decomposition are presented.

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