Crystallization-induced asymmetric synthesis of nonracemic platinum(IV)polysulfide tris(chelate) complexes.

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The random nonracemic formation of the platinum(IV) polysulfide tris(chelate) anionic complex $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$, previously believed to be due to a crystallization-induced asymmetric transformation of the reaction product, under scrutiny turned out to be a new type of autocatalytic asymmetric synthesis. The synthesis is driven by simultaneous crystallization of the product as an enantiomorphous conglomerate. In particular, the preparation becomes chemo- and stereoselective when carried out with continuous vigorous stirring in the presence of seeds of the desired nonracemic ultimate reaction product, i.e. an autocatalyst. However, structural characterization of the randomly obtained products by means of XRD, ^{195}Pt NMR, and ESI-MS measurements as well as X-ray single-crystal analyses, reveals the significant complexity of the reaction. Several tris(polysulfide) congeners and their stereoisomers are usually obtained, and they may even cocrystallize. All these characteristics point to the kinetic control of these autocatalytic asymmetric preparations under the applied nontrivial reaction conditions. Consequently, the composition and handedness of the products can to a large extent be controlled by seeding the reaction mixture with a small previously obtained solid sample, which contributes to the synthesis as an autocatalyst.

Słowa kluczowe

asymmetric synthesis, conglomerates, autocatalysis, platinum, polysulfides

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