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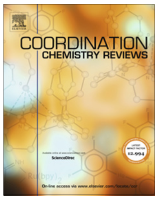

Review

Engineering solid state structural transformations of metal complexes

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ABSTRACT

Solid state reactivity and structural transformation involving metal complexes driven by non-photochemical conditions are presented in this review. The single crystals preserved at the end of most of the reactions are discussed. These single-crystal-to-single-crystal (SCSC) reactions involving bond-breaking and making process by the non-photochemical routes are usually triggered by exposure of solvent vapors and gases, removal or exchange of solvents and guest molecules, heat, or their combinations. The structural transformations of simple metal complexes, metallamacrocycles, organometallic compounds and cages, for example, involve phase transitions accompanied by change in metal-metal bonding distances, change in coordination sphere and geometry, molecular association from monomers and dimers to tetramers and polymers, molecular rearrangements and isomerization, unexpected reactivity that were unknown in solution, and change of chirality.

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1. Introduction

The restricted movement of molecules in the solid state is often a stumbling block in conducting reactions in the solid state, even though the solventless approach is environmentally benign [1–5]. Hence, reactions of coordination metal complexes and organometallic compounds are usually conducted in solution. On the contrary, the absence of the influence of the solvents may provide unique products that were not normally accessible in solution. For example, the restricted movements of the predisposed molecules can yield unexpected and unusual as well as regio- and steroselective products due to the absence of freedom in the solid state [6,7]. If the reactive functional groups are already juxtaposed close to the transition state, then the reaction can easily be carried out in the solid state. This has been abundantly demonstrated in the solid state [2+2] cycloaddition reactions where a pair of olefins has been successfully aligned using crystal engineering principles [8–24]. Therefore, the molecules need not have to move very far during these topochemical reactions. The reaction in which the single crystals are retained in the product is called SCSC transformation [25,26]. Direct observation of molecular movements in the lattice from the SCSC reaction enables to derive the mechanistic details of the structural transformation to be derived. Thus the SCXRD technique is still the ultimate and exclusive tool available to monitor these solid-state reactions [26–35].

The SCSC reactions are prevalent in coordination polymers and metal-organic framework structures [27–35]. The porous structure with channels and empty cavities in these solids can allow the reactants and products to travel and escape without affecting the robust framework structures. Due to the lack of robustness, it may not be possible in the discrete zero-dimensional metal complexes to maintain the single crystal of the product. If the SCSC reaction fails, then PXRD patterns of the reaction products should be matched satisfactorily with those simulated patterns from the single crystal data. However, recrystallization of the products may yield different phase due to the influence of the crystallization conditions. Hence sometimes, this may not be as elegant as the SCSC reactions. This review presents the non-photochemical solid-state reactions involving discrete coordination metal complexes and organometallic compounds. Further SCSC reactions have been discussed mostly with some exceptions. The number of solid-solid, solid-liquid and solid-gas reactions are enormous and are usually dealt under solid state reactions and materials syntheses in general. There are several reviews on mechanochemical reactions [3,36–39]. As we focus on the SCSC reactions, these are not covered extensively in this review. Recently, a review was published on the supramolecular transformations of discrete coordination-driven supramolecular architectures in solution [40] which complements this review. Although the literature covered is fairly comprehensive, to the best of our knowledge, it is by no means complete. A separate review on the photoreative photochemical reactions of metal complexes will be published elsewhere.

2. Polymorphic changes

Traditionally polymorphism has been extensively investigated in inorganic compounds with extended network structures like metal oxides, sulfides and phosphates. In recent times, it is gaining importance in organic compounds due to its relevance to pharmaceutical industries. Nonetheless, polymorphism in metal complexes has mainly been explored as a curiosity driven research so far. The transformation among some of the polymorphic phases are accompanied by thermochromism, vapochromism, thermolunescence, piezochromism, mechanochromism, and magnetochromism.

Different polymorphs of gold(I) complexes that differ in their Au···Au distances are known to interconvert upon changes in temperature. Some of them show distinct luminescence properties before and after the transition [41–45]. For example, yellow polymorphs of $[(C_6H_{11}NC)_2Au](PF_6)$ and $[(C_6H_{11}NC)_2Au](AsF_6)$ are converted to colorless forms upon exposure to the vapors of dichloromethane, acetone, methanol or acetonitrile [46]. Further, the vapors of diethylether, water, or pentane do not produce any change to the yellow, green-glowing polymorphs. When a mixture of these solvents was used for crystallization, the yellow polymorphs grew in diethyl ether-rich regions, and diethyl ether vapor has no effect on this polymorph. In contrast, the colorless, blue glowing form grew in dichloromethane-rich regions, and dichloromethane vapor converts the yellow, green-glowing polymorph into the colorless, blue-glowing polymorph. The colorless form can be converted to yellow form upon heating at 98–102 °C. In the colorless polymorph, all the Au(I) atoms are aligned in a straight line while the yellow form has a corrugated alignment of its Au(I) atoms.

A very similar gold(I) compound, phenyl(phenyl isocyanide)-gold(I) exhibited mechanochromism when a small mechanical force was applied on the surface of the single crystals of the metastable phase with space group $P\bar{1}$ (Fig. 1) and undergo SCSC transformation to a more stable phase (space group I-42d). This mechanochromic phase transformation is accompanied by a dramatic shortening of the Au···Au distance from 5.733 Å to 3.177 Å as well as the red-shifting of the PL spectrum from blue (λ_{max} = 460 nm excited at 315 nm) to yellow (λ_{max} = 565 nm excited at 432 nm) [47]. This compound as well as their derivatives have been extensively explored for their mechnochromism [48–51].

Two pseudo polymorphic phases of $[Pt_2(bipy)_2(\mu\text{-}P_2O_7)]$ were synthesized independently by two different methods [52]. The deep green crystals (space group $C2/c$) with 3.5 lattice water can be transformed in an SCSC manner to the orange form (space group Cc) with 6 lattice water molecules by exposure to air or water in an SCSC manner. But the reversible transformation only occurs partially when the compound is dried in vacuo. The Pt···Pt distances in the dimers are slightly different (3.0318(6) Å in the green form and 3.0522(3) Å in the orange form). The dimeric complexes in the green form are related by center of inversion with inter-dimer Pt···Pt distance of 3.12 Å, while the dimers in the orange form are twisted by 60° relative to each other along the c-axis with Pt···Pt distance of 4.56 Å (Fig. 2).

Orange elongated hexagonal-shaped crystals and green diamond-shaped crystals of $[(CH_3)CHNH_3]_2[Cu_2Br_6]$ can be

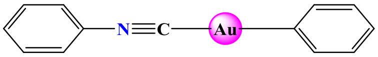

Fig. 1. Gold(I) compound exhibiting mechanochromism [47].