

Synthesis, X-ray structural characterization and pyrolysis studies of heterobi- and heterotrimetallic molecular complexes

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Abstract Heterobi- and heterotrimetallic complexes $[\text{NiTi}(\text{acac})_2(\text{dmae})_2]_2$ (**1**) and $[\text{Ba}(\text{acac})(\text{OH})_2\text{Ni}_2(\text{acac})_4\text{Ti}(\text{dmae})_2]$ (**2**) (acac = acetylacetonate, dmae = *N,N*-dimethyl aminoethanolate) have been synthesized by simple reactions of Ni(II) acetylacetonate, Tl(I) acetylacetonate and dmaeH for (**1**) and Ni(II) acetylacetonate, Tl(I) acetylacetonate, Ba metal and dmaeH for (**2**) in toluene to obtain crystalline products that were characterized by physicochemical and spectroscopic methods. Single-crystal X-ray analysis of both complexes shows that they crystallize in a monoclinic crystal system with space group $P2_1/c$. TGA studies of the complexes indicate that complex (**1**) is a suitable precursor for the preparation of composite $\text{NiO}/\text{Ti}_2\text{O}_3$, while complex (**2**) yields an unstable composite $\text{NiO}/\text{Ti}_2\text{O}_3/\text{BaO}$ which on exposure to air is converted to $\text{NiO}/\text{Ti}_2\text{O}_3/\text{BaCO}_3$ by the absorption of atmospheric carbon dioxide.

Introduction

Recently, considerable attention has been focused on the synthesis of heterometallic complexes in which different metal centers are bonded through bridging donor atoms such as O, N and S. Such molecular complexes provide a direct route to the synthesis of multimetallic ceramic composites for high-tech industrial applications. For the synthesis of these complexes, the choice of proper ligands plays an important role. In this regard, several bi- and tridentate ligands such as amino alcohols, acetylacetonate, acetate and fluoroacetate, have been used to form molecular species such as $[\text{CuCoZn}_2(\text{Dea})_3\text{Cl}_3(\text{HOMe})]\cdot\text{MeOH}$, $[\text{CuCoZn}(\text{Me}_2\text{Ea})_4(\text{NCS})_2(\text{OAc})]$ [1] (H_2Dea = diethanolamine and HMe_2Ea = 2-(dimethylamino)ethanol), $[\text{Cu}_2\text{CoPbCl}_4(\text{L})_4]_2$ and $[\text{Cu}_2\text{CoCd}_2\text{Cl}_6(\text{L})_4(\text{HOMe})_2]$ [2] (L = 2-dimethylaminoethanolate).

As far as thallium heterometallic chemistry is concerned, a few examples of its complexes with transition metals such as gold and titanium have been reported in the past [3–6]. For example, an Au(I)-Tl(I) complex was prepared by the reaction of $\text{M}[\text{AuR}_2]$ with a Tl(I) salt to yield $[\text{Au}_2\text{Tl}_2\text{R}_4]\cdot(\text{CH}_3)_2\text{CO}$ (where M = alkali metal or Bu_4N ; R = C_6H_5 , C_6Cl_5) [3, 4], and a variety of double alkoxides with different stoichiometries of thallium and titanium have been reported [5]. The unusual properties of thallium complexes [7, 8] attributed to the relativistic disturbance of the $6s^2$ electrons, provided the background of our interest in the synthesis of its bimetallic complexes with nickel and its successful use as a template for a more complex extended trimetallic geometry. The introduction of barium (*s*-block) into the Ni/Tl framework of complex (**1**) is of particular interest in order to study the “one-pot” syntheses of these precursors. Here, we report the synthesis and X-ray characterization of the heterobi- and heterotrimetallic

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