THE PROBLEM OF THE STORAGE OF ALKALINE EARTH PRECURSORS CONTAINING 2,2,6,6-TETRAMETHYLHEPTANEDIONE-3,5

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The problem of storage of alkaline earth metal derivatives of 2,2,6,6-tetramethylheptanedione-3,5 (**Hthd**) has been studied. For such study we have chosen the mixed ligand complexes with **thd** and a pyrazole, as neutral Lewis base, able to coordinate the central atom in neutral form. Such precursors have the advantage of a low content of carbon, with respect to other Lewis bases already used to protect alkaline-earth metal center from hydration and hydrolysis, which diminishes the carbon contamination of films. The coordinated ligand in such complexes usually undergoes a partial cleavage during a period of two-three months giving non-crystalline products. We succeeded in crystallization of one of such products in the form of heterobimetallic complex by addition of a titanium precursor.

The reaction of strontium and barium with **Hthd** and pyrazole gives mononuclear strontium and dinuclear barium derivatives with the azole acting as neutral ancillary ligand. The formation of adducts with pyrazole stabilizes barium toward hydrolysis with respect to $\mathbf{Ba_4(thd)_8}$. Both complexes are volatile in vacuo. On sublimation at 10^{-3} torr they dissociate on alkaline-earth diketonate and pure pyrazole. The TG curves are given in Figure 1.

The strontium complexes are shown to be sufficiently sensitive to hydrolysis. On the basis of spectroscopic and structural data it was shown that hydrolysis causes the cleavage of *thd*-ligand to pivalate and ketoalcohol followed by the formation of pivalate-containing oligomeric species. The addition of $\mathbf{Ti(^iPrO)_2(thd)_2}$ made it possible to crystallize a product of hydrolysis in the form of heterobimetallic derivative $\mathbf{\{[Ti(thd)_2(\mu^3\text{-}O)(\mu\text{-}Bu^tC(O)CH_2CH_2O)Sr(thd)(\mu\text{-}Bu^tCOO)]_2Sr(Hpz)_2\}}$. Its' crystal structure has been resolved (Figure 2) The arrangement of Sr3 fragment in its' structure is similar to that in unhydrolyzed $\mathbf{Sr_3(thd)_6}$.

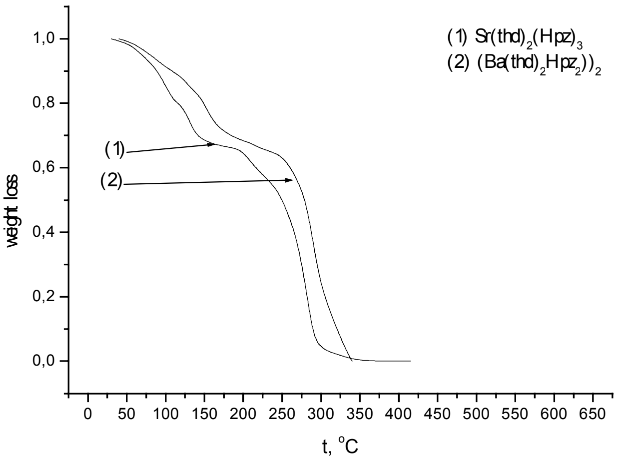

Figure 1

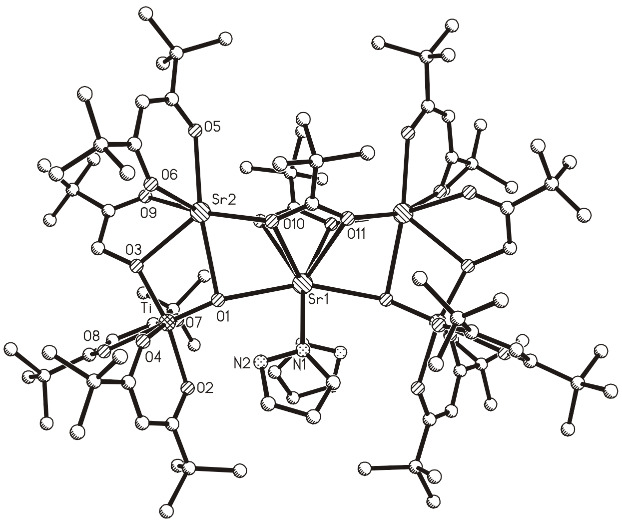

Figure 2

References
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