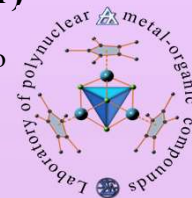




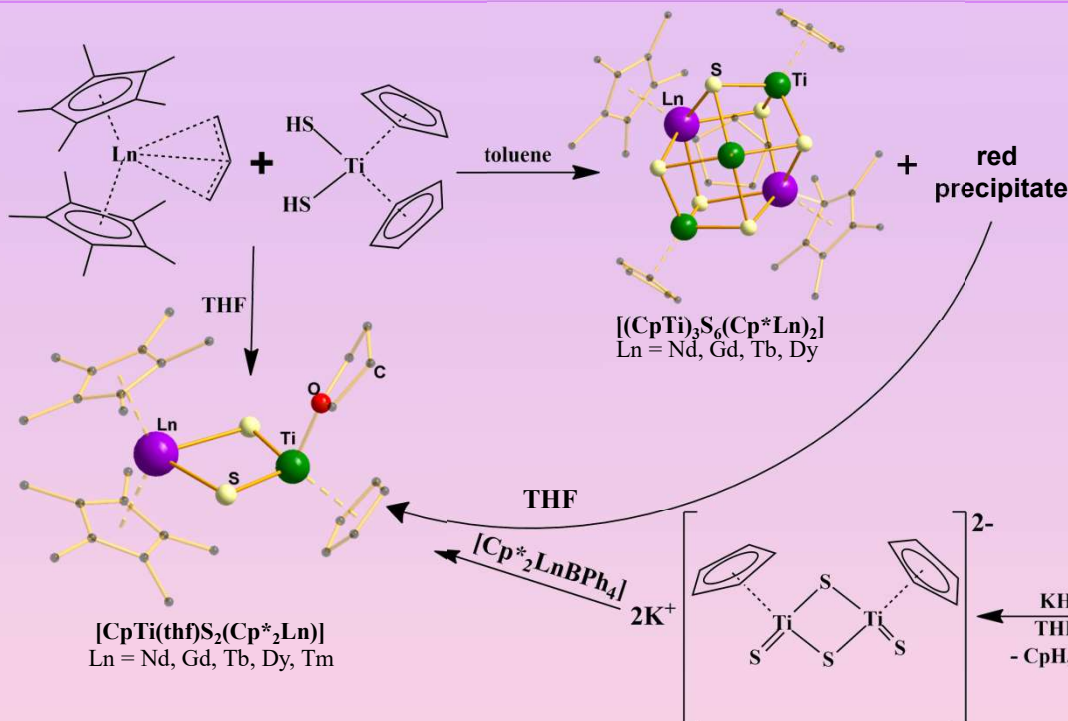
Acid-base approach to the synthesis of heterometallic chalcogenide complexes of lanthanides and transition metals (Ni, Ti, Zr)

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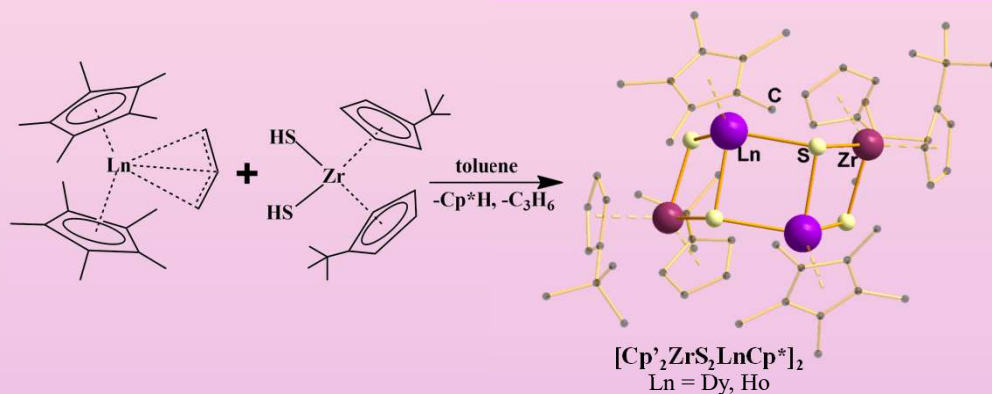


Heterometallic complexes of lanthanides with transition metals are promising objects for research. Such compounds may have exceptional catalytic, unusual magnetic and luminescent properties. Few heterometallic *d/f* chalcogenide complexes are known; therefore, the development of methods for the synthesis of such compounds is an urgent task. In this work, we proposed a new synthetic approach based on the acid-base interaction.



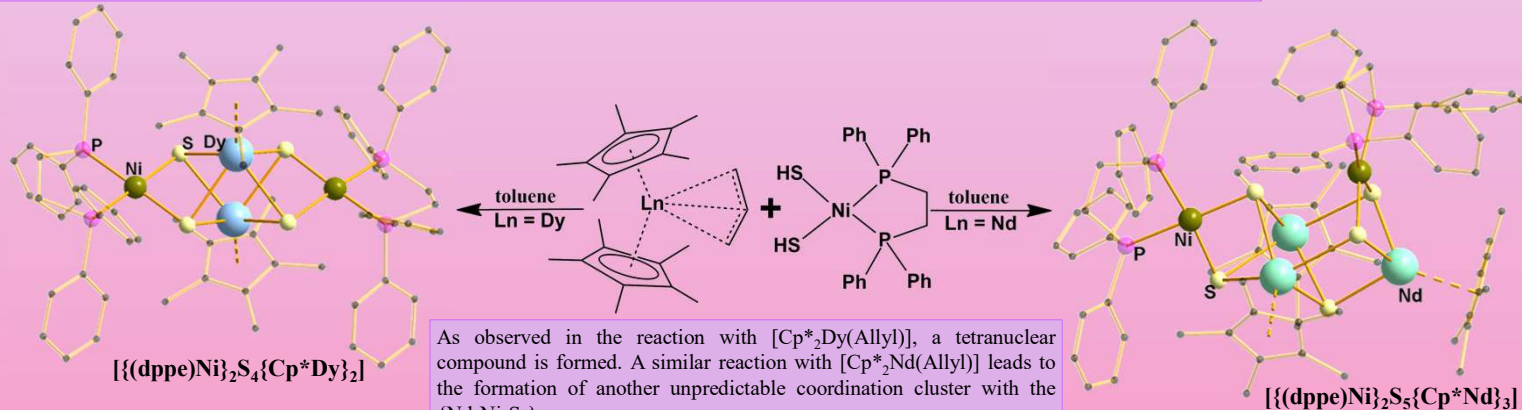
Reactions of $[\text{Cp}^*_2\text{Ln}(\text{Allyl})]$ with the titanium complex $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ result in two substantially different products, depending on the chosen solvent: in toluene, a five-nuclear cluster is formed; in THF, a binuclear complex is formed.

We have developed another method for the selective preparation of the binuclear complex. It is known that a dimeric anionic complex is formed in the interaction of KH with $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ (B. L. Scott et al // *Organometallics*, Vol. 15, No. 17, 1996). We carried out the reaction *in situ*, and the resulting product was investigated in the reaction with a $[\text{Cp}^*_2\text{LnBPh}_4]$. In this case, the binuclear complex is formed selectively and in high yield (~90%).



The use of a similar zirconium complex $[\text{Cp}'_2\text{Zr}(\text{SH})_2]$ in reactions with $[\text{Cp}^*_2\text{Ln}(\text{Allyl})]$ leads to the formation of fundamentally different products. For dysprosium and holmium, the obtained compounds are isostructural.

The $[(\text{dppe})\text{Ni}(\text{SH})_2]$ complex of nickel has a chelate diphosphine ligand in its structure, and unlike $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ complex, where the protonation of the cyclopentadienyl ligand occurs, such a process is impossible here. In our view, this should have led to more predictable products.



As observed in the reaction with $[\text{Cp}^*_2\text{Dy}(\text{Allyl})]$, a tetranuclear compound is formed. A similar reaction with $[\text{Cp}^*_2\text{Nd}(\text{Allyl})]$ leads to the formation of another unpredictable coordination cluster with the $\{\text{Nd}_3\text{Ni}_2\text{S}_5\}$ core.

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