



Research paper

Control of the composition and crystal structure of exchange reaction products of rare-earth acetates with pivalic acid



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ABSTRACT

The rare-earth metal(III) complexes $[M_2(\text{piv})_6(\text{Hpiv})_6]$ (monoclinic, $P2_1/c$, **1**), $[M_2(\text{piv})_6(\text{Hpiv})_6]\cdot\text{Hpiv}$ (monoclinic, $C2/c$, **2**), $[M(\text{piv})_3]_n$ (trigonal, $P6_3/m$, **3**), and $[(\text{Hpiv})_2(\text{PrOH})_2\text{Sm}_2(\text{piv})_6]\cdot 2\text{Hpiv}$ (triclinic, $P-1$, **4**), where piv is $(\text{CH}_3)_3\text{CCO}_2^-$, were synthesized, and their structures were determined by single-crystal X-ray diffraction (SC-XRD). The crystallization was shown to be controllable by varying the nature of the salting-out agent – the non-coordinating organic solvent in the $M(\text{OAc})_3\cdot 4\text{H}_2\text{O}\text{--}\text{Hpiv}$ system. The following bulky single-phase samples were obtained: dimers **1** or **2** with $M = \text{Pr, Nd, Sm, Eu, and Gd}$ using hexane C_6H_{14} ; dimer **1** or 1D polymer **3** with $M = \text{Y, Er, and Yb}$ using EtOH; dimers **2** or **4** with $M = \text{Sm}$ using $^i\text{PrOH}$. A reversible phase transition to a commensurate modulated modification ($P2_1/c$) was observed for crystals of **1** (P_n). The magnetic properties of complexes **1a** (Pr), **1b** (Nd), **4** (Sm), **1d** (Eu), **1f** (Dy), **1g** (Ho), and **1h** (Er) were investigated.

1. Introduction

The exchange reaction of rare-earth acetates with pivalic acid holds a special place among numerous methods for the synthesis of polynuclear rare-earth carboxylate complexes [1–11]. In this reaction, pivalic acid serves not only as a source of new O-donor ligands but also as an organic solvent, which, on the one hand, makes it possible to perform the synthesis at elevated temperatures (100 °C and higher) with almost no decomposition of metal-containing derivatives and, on the other hand, allows the isolation of the reaction products in the crystalline state in rather high yields. Earlier, this approach was used to synthesize a series of rare-earth pivalates with different metal centers, such as La [12], Ce [13], Pr [13], Nd [13], Sm [12,14], Eu [12,14], Gd [14,15], Tb [15], EuTb [16], Dy [3,13], Ho [13], Tm [17], and Er [13,14], of different composition and structure. The nature of the crystals of the resulting pivalate complexes largely depends not only on the method of synthesis but also on the procedures used for the isolation of the final products, which, in turn, depend on different factors. Thus, binuclear complexes $[M_2(\text{piv})_6(\text{Hpiv})_6]$ (**1**) [13,15,16], their solvates with pivalic acid $[M_2(\text{piv})_6(\text{Hpiv})_6]\cdot\text{Hpiv}$ (**2**) [12–14], or even unsolvated coordination polymers $[M(\text{piv})_3]_n$ (**3**) [14,15,17], which have significantly different structures and properties, were isolated using metals of different nature and additional salting-out agents,

changing the time during which the reaction mixture was stored, and varying some other factors. It should be remembered that the metal-core structure of polynuclear carboxylate complexes of rare-earth metals(III), in particular, pivalates, which are usually binuclear [18–21] or polymeric [2,22–26] molecules, can be varied in a wide range mainly due to the ability of carboxylate anions to exhibit various structural functions, from monodentate terminal to μ_4 -bridging. Nevertheless, the electronic nature and geometric parameters of the metal ion and the carboxylate anion should also be taken into account. These factors can be employed to affect the chemical and physical properties of the resulting polynuclear architectures, including magnetic and luminescence characteristics. Evidently, the physical properties of these systems are mainly determined by the metal centers; however, for example, the magnetic characteristics of the complexes to a large extent depend not only on their molecular structure but also on the crystal structure. Rare-earth carboxylate (in particular, pivalate) complexes are extensively studied coordination compounds due to their unique magnetic, optical, catalytic, absorption, and other important physical properties and also because of their promising applications in modern technologies as components of functional materials [1,27–35]. Therefore, the development of efficient procedures for the preparation of such molecular materials of identical composition and structure is an important issue.

In the present work, we studied in detail the exchange reaction of

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aqueous rare-earth acetates with pivalic acid (the $M(\text{OAc})_3 \cdot 4\text{H}_2\text{O} \text{--} \text{Hpiv}$ system, where $M = \text{Y, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb}$), and examined the feasibility of dimer \leftrightarrow solvated dimer and dimer \leftrightarrow polymer transitions in this reaction in the presence of salting-out agents – hexane (C_6H_{14}) as a non-coordinating organic solvent or monatomic saturated alcohols EtOH and $^i\text{PrOH}$, which are weak Lewis bases. In addition, the magnetic properties of the known and new polynuclear rare-earth pivalates, which were isolated in this study or prepared by other methods, were investigated.

2. Results and discussion

2.1. Synthesis and X-ray diffraction study

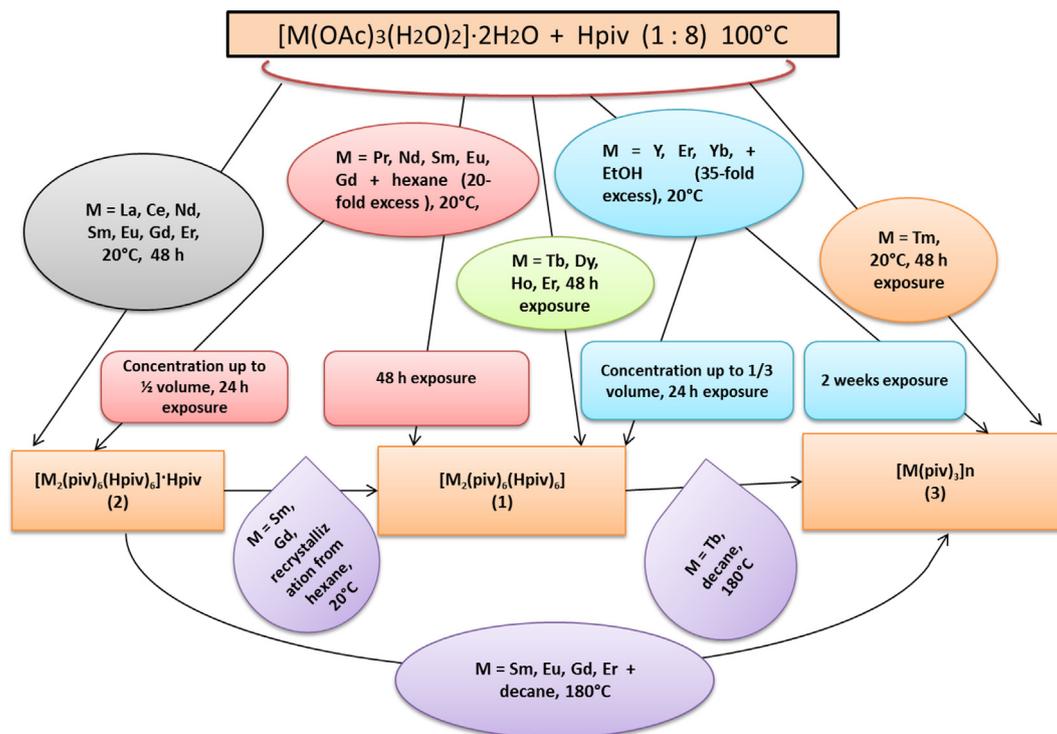
Recently, we have reported that the $M(\text{OAc})_3 \cdot 4\text{H}_2\text{O} \text{--} \text{Hpiv}$ reaction system is promising for the one-step synthesis of single-phase single-crystalline binuclear rare-earth metal complexes $[\text{M}_2(\text{piv})_6(\text{Hpiv})_6]$ (**1**) or $[\text{M}_2(\text{piv})_6(\text{Hpiv})_6] \cdot \text{Hpiv}$ (**2**) in nearly quantitative yields [3,12–16]. Complexes of type **2** were prepared with La [12], Ce (**2a**) [13], Nd (**2b**) [13], Sm (**2c**) [12], Eu (**2d**) [12], Gd (**2e**) [14], and Er [14], dimers **1** were obtained with Tb [15], EuTb [16], Dy (**1f**) [13,3], Ho (**1g**) [13], and Er (**1h**) [13], dimers **1** with Sm (**1c**) and Gd (**1e**) were prepared by recrystallization of appropriate complexes **2** from hexane (C_6H_{14}) [14] (Scheme 1). In addition, crystals of the binuclear unsolvated complex $[\text{M}_2(\text{piv})_6(\text{Hpiv})_6]$, where M is Y (**1i**), were obtained by the exchange reaction of yttrium carbonate with an excess of Hpiv [9], and crystals of the related complexes with Ce [10,11] and Nd (**1b**) [11] were prepared by the reaction of aqueous lanthanide carbonates with Hpiv or of lanthanide nitrates with an aqueous ammonia solution in the presence of Hpiv followed by the crystallization of the reaction products from C_6H_{14} or a Hpiv– C_6H_{14} mixture. In the work [3], crystals of the Dy complex (**1f**) were prepared by the reaction of Dy_2O_3 with an excess of Hpiv followed by the recrystallization of the reaction product from a toluene–hexane mixture.

We found that the addition of hexane to the reaction mixture produced upon the thermal treatment of the $M(\text{OAc})_3 \cdot 4\text{H}_2\text{O} \text{--} \text{excess Hpiv}$

system and subsequent storage of the mother liquor in air at room temperature for 48 h also afforded single-phase single crystals of pivalates **1** with Pr (**1a**) [13], Nd (**1b**), Sm (**1c**), Eu (**1d**), and Gd (**1e**) (Scheme 1). The removal of C_6H_{14} from the mother liquor, for example, by concentrating under reduced pressure, gives rise to crystals of solvate **2**. Therefore, the crystallization proved to be a controllable process, the dimer **1** \leftrightarrow solvated dimer **2** transition being controlled by C_6H_{14} .

It should be noted that, in some cases, the piv anions containing the branched electron-donating *tert*-butyl moiety can shield the inner coordination sphere of rare-earth metal atoms, thus preventing the reaction with neutral donor ligands, such as H_2O or Hpiv molecules. This ensures the preparation of coordination-deficient polymeric carboxylates. Actually, the use of the $\text{Tm}(\text{OAc})_3 \cdot 4\text{H}_2\text{O} \text{--} \text{excess Hpiv}$ reaction system results in the formation of single crystals of the 1D coordination polymer $[\text{Tm}(\text{piv})_3]_n$ (**3a**) in nearly quantitative yield [17] (Scheme 1). By contrast, the complete removal of coordinated Hpiv molecules from binuclear pivalates **1** or **2** upon thermolysis in decane ($\text{C}_{10}\text{H}_{22}$) at 180°C gave rise to polycrystalline polymeric pivalates of the composition $[\text{M}(\text{piv})_3]_n$ (**3**), where M is Sm [14], Eu [14], Gd [14], Tb [15], or Er [14] (Scheme 1). The thermal decomposition of related binuclear rare-earth metal complexes under an inert atmosphere at $180\text{--}200^\circ\text{C}$ afforded pivalates **3** with Y (**3b**) [36] and Er (**3c**) [37].

Unexpectedly, the addition of EtOH to the reaction mixture, which was obtained after the above-mentioned thermal reaction involving $M(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ ($M = \text{Y, Er, Yb}$) and an excess of Hpiv, and variation of the crystallization conditions were found to have a significant effect on the composition of the resulting crystals (Scheme 1). Thus, the storage of this mixture in air at ambient temperature for 2 weeks results in the crystallization of isomorphous Y and Er pivalates (**3b** and **3c**, respectively) and the previously unknown Yb pivalate (**3d**), which do not contain coordinated neutral Hpiv, EtOH, or H_2O molecules. According to powder X-ray diffraction (PXRD), the crystals of all polymeric pivalates are single-phase products. The gas chromatography–mass spectrometry (GC–MS) analysis demonstrated (correlation coefficient 0.98) that the reaction solution contained ethyl 2,2-dimethylpropionate



Scheme 1. Formation pathways of the pivalate complexes $[\text{M}_2(\text{piv})_6(\text{Hpiv})_6]$ (**1**), $[\text{M}_2(\text{piv})_6(\text{Hpiv})_6] \cdot \text{Hpiv}$ (**2**), and $[\text{M}(\text{piv})_3]_n$ (**3**) in the $M(\text{OAc})_3 \cdot 4\text{H}_2\text{O} \text{--} \text{excess Hpiv}$ reaction system.

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