

Supplementary Material

Crystal structure of the dodecanuclear coordination compounds [RE₁₂(DMF)₂₄(HCOO)₈(OH)₁₆]I₃·4DMF (RE = Eu, Nd)

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Detailed synthesis protocol for [Eu(DMF)₈]I₃ and [Nd(DMF)₈]I₃

(*RE* = Eu and Nd) were prepared starting from N,N-dimethylformamide (DMF) solutions of the respective iodide solvates [*RE*(DMF)₈]I₃.

Fuming HCl (37%, 20 mL) was heated to 85 °C and Eu₂O₃ (10.0 g, 28.4 mmol, Acros Organics, 99.5%) was added in small portions of 0.5 g until a cloudy suspension no longer cleared up within 30 min. The excess of Eu₂O₃ was dissolved by dropwise addition of fuming HCl. After cooling the solution to room temperature, water was removed under reduced pressure yielding colorless crystals of [Eu(H₂O)₆]Cl₃. A portion thereof was dissolved in DMF (150 mL) and a solution of 29.3 g (177 mmol, large excess) KI in 35 mL dry DMF was added. Immediately, a colorless precipitate of KCl formed and was filtered off. To the remaining solution 50 mL of toluene were added and an azeotropic distillation on a Dean-Starck apparatus under reflux conditions was carried out. The now pale yellow solution was cooled to room temperature and the crystalline product was collected. The product was recrystallized from DMF. [Eu(DMF)₈]I₃ was formed as big cuboid colorless crystals and was identified by single crystal diffraction. Purity of the product was checked by powder diffractometry. In the same manner crystalline [Nd(DMF)₈]I₃ was prepared. The crystalline Nd compound shows the typical pleochroism: in sunlight the crystals appear pale purple and pale yellow under fluorescent light.