Chinese Journal of Chemistry 2006 24 (08): 1013-1019 ISSN: 0567-7351 CN: 31-1320/06

Full Papers

三元配合物**RE [(Pdtc)$_3$(phen)]**热化学性质的规律性

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收稿日期 2005-8-9 修回日期 2006-4-11 网络版发布日期 2006-8-29 接受日期

摘要 在无水乙醇中，用吡咯烷二硫代氨基甲酸铵（$C_5H_8NS_2$，APDTC）和1,10-邻菲咯啉($C_{12}H_8N_2$， o-phen·H_2O)分别与13种低水合氯化稀土合成了三元固态配合物，确定它们的组成可用通式RE(Pdtc)$_3$(phen) (RE=La, Pr, Nd, Sm-Lu)表示。用RD496-Ⅲ微量热计测定了298.15 K下13种水合氯化稀土盐及两个配体在无水乙醇中的溶解焓，两个配体醇溶液的混合焓及13种化合物液相生成反应的焓变，并通过合理的热化学循环，求得了标题配合物的固相生成反应焓变；推导了用RD496-Ⅲ型微热量计测定固态物质比热容的计算式并测定了标题配合物298.15 K的比热容。发现系列配合物RE(Pdtc)$_3$(phen)（RE=La、Pr、Nd、Sm~Lu）的多项热化学性质，如低水合氯化稀土盐在无水乙醇中的溶解焓以及配合物的液相生成反应焓变和固相生成反应焓变、常温比热容、标准摩尔燃烧焓和标准摩尔生成焓都与稀土原子序数作图呈现“三分组现象”。较集中地反映出配合物中RE^{3+}与配体间的化学键有一定程度的共价性，这是由于稀土离子$5s^25p^6$轨道对4f电子的不完全屏蔽引起的。

关键词 RE(Pdtc)$_3$(phen), 热化学性质, 三分组现象, 规律性

分类号

Regularity of Thermochemical Properties of Ternary Complexes RE[(pdtc)$_3$(phen)]

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Abstract Treatment of hydrate rare-earth (RE＝La, Pr, Nd, Sm-Lu) chloride with ammonium pyrrolidinyldithiocarboxylate (apdtc) and 1,10-phenanthroline (phen) gave rise to thirteen complexes with an empirical formula RE[(pdtc)$_3$(phen)]. The enthalpies of solution of hydrate rare-earth (RE＝Sm-Ho, Tm-Lu) chloride, apdtc and phen in ethanol were measured by an RD-496 III microcalorimeter at 298.15 K, along with the mixing enthalpy of ethanol solution of APDC and that of phen and the enthalpies of reaction of formation of the title complexes in ethanol. The enthalpies of reaction of formation of the title complexes in solid were available through a rationally thermochemical cycle. Using an RD-496 III microcalorimeter, a model was developed for calculating the specific heat capacity and the responding specific heat capacity of the complexes were determined. The thermochemical properties, including the enthalpies of solution of hydrate rare earth chloride in ethanol, the enthalpies of reaction of formation of the title complexes in ethanol, the enthalpies of reaction of formation of the title complexes in solid, the special heat capacities at room temperature, the standard molar enthalpies of combustion and the standard molar enthalpies of formation for this series of complexes versus the atomic numbers of rare earth, presented triplet effect, which is representative of certain covalent bond between RE and the ligands and the result of 4f electron not shielded fully by 5s5p.

Key words RE[(pdtc)$_3$(phen)] thermochemical property triplet effect regularity

DOI:

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