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Introduction: Frontiers in Lanthanide Chemistry

Lanthanides are elements of rapidly growing importance. They are part of the family of rare earths, which also includes scandium, yttrium, and lanthanum. This thematic issue is mainly concerned with lanthanides, hence the brief and focused title. The availability of lanthanides at quite cheap prices facilitates their use in chemistry and applications. Much progress has recently been achieved in the coordination chemistry of lanthanides, in the use of lanthanide-based reagents or catalysts, and in the preparation and study of new materials. The thematic issue is a timely enterprise, which covers a large body of new advances presented by experts and specialists of these various fields. The 22 articles may be broadly classified into three groups: coordination chemistry of lanthanides (synthesis and structure of complexes), organic transformations mediated or catalyzed by rare-earth compounds, and finally the preparation and properties of new materials or sensors.

The first category (coordination chemistry) includes seven contributions. Aspinall describes the coordination chemistry of chiral lanthanide complexes as well as their application in catalysis. Edelmann, Freckmann, and Schumann present the synthesis and structures of non-cyclopentadienyl organolanthanides, describing the many classes of complexes (mainly Ln(II) and Ln(III)) now known. Bünzli and Piguet show how lanthanides can be involved in polymetallic assemblies thanks to polydentate ligands and supramolecular chemistry. The authors emphasize the importance of lanthanide ions as optical spectroscopic or magnetic probes for various applications. Mitchell and Ibers review the area of mixed rare-earth transition-metal chalcogenides which have been characterized by single-crystal diffraction methods, while Arndt and Okuda present the family of mono(cyclopentadienyl) rare-earth complexes together with applications in homogeneous catalysis. Parker, Dickins, Puschmann, Crossland, and Howard examine the structure and various aspects of the photochemistry or chiroptical properties of lanthanide complexes in aqueous solution. Wickleder concentrates on inorganic lanthanide compounds (devoid of organic ligands) involving complex anions and provides many X-ray single-crystal structures.

The second group of articles (organic transformations controlled by lanthanide derivatives) includes papers which remain mainly oriented toward coordination chemistry or which are basically concerned by the efficiency and selectivity of organic transformations. Bochkarev details the synthesis and identification of arene−lanthanide compounds (Sc and Y are also included) as well as their chemical reactivities. The divalent lanthanide derivatives are widely used in organic synthesis, especially diiodosamarium, a reagent that we introduced in organic chemistry more than 20 years ago (*J. Am. Chem. Soc.* **1980**, *102*, 2693). Since several reviews in this journal have summarized recent developments (*Chem. Rev.* **1992**, *92*, 29; *Chem. Rev.* **1996**, *96*, 307; *Chem. Rev.* **1999**, *99*, 745), it was decided not to include this important area in this special issue. Evans and Davis present the chemistry of $(Me_5C_5)_3Ln$ complexes, a quite new chemistry, as until 1991 it was believed these compounds could not exist. Marques, Sella, and Takats similarly discuss the structure and chemistry of divalent and trivalent lanthanide complexes involving pyrazolylborate ligands. Catalysis by lanthanide complexes is a highly promising area that is covered by four contributions. Molander and Romero show the importance of lanthanocene catalysts to perform selective organic synthesis. This paper is organized by reaction types (hydrogenation, hydrosilylation, hydroboration, etc.). Shibasaki and Yoshikawa describe for various enantioselective reactions the wide scope of bifunctional asymmetric lanthanide(III) catalysts, mostly heterobimetallic complexes based on lanthanide and alkali metal. Chiral lanthanide catalysts giving rise to asymmetric amplifications (nonlinear effect) are reviewed by Inanaga, Furuno, and Hayano. Kobayashi, Sugiura, Kitagawa, and Lam explore the numerous developments in catalytic organic synthesis arising from the Lewis-acid properties of rare-earth metal triflates.

The third group of contributions is devoted to many different kinds of materials or sensors using lanthanide components. Binnemans and Görller-Walrand present the synthesis, structure, and physical properties of liquid crystals and surfactants containing lanthanides. Kuriki, Koike, and Okamoto review the use of lanthanide complexes in optical fiber lasers

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and amplifiers, while the paper by Kido and Okamoto is devoted to electroluminescent materials based on organolanthanide complexes. Benelli and Gatteschi discuss the magnetism of lanthanides in molecular materials with transition-metal ions and organic radicals. Properties of lanthanide complexes are very useful in molecular recognition and chirality sensing of biological substrates, as explained by Tsukube and Shinoda. Adachi, Imanaka, and Tamura review the topic of ionic conductive lanthanide oxides. Lombardi and Davis present the periodic properties of force constants of small transition-metal and lanthanide clusters. Finally, Adam discusses the interest of lanthanide components in non-oxide glasses.

The present importance of lanthanides is clearly evidenced by the rich and diversified chemistry which has been reviewed by 50 authors and co-authors, generating 3700 references and notes, and 670 printed pages. The multidisciplinary character of lanthanide research is well illustrated in this special thematic issue, since the topics range from inorganic and organometallic chemistry through organic chemistry and from physics to biology. Moreover, lanthanides remain very topical in material sciences. It is expected that this thematic issue will stimulate research in all of these areas, where we can expect many more exciting discoveries. The guest editor thanks the authors for having agreed to participate in this enterprise and for their excellent contributions. He also thanks Professor Gladysz and Ms. Haltrich from *Chemical Reviews* for their kind and efficient support.

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