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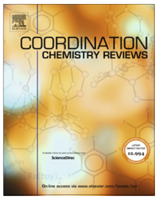

Review

Rare earth metal-containing ionic liquids

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ABSTRACT

As an innovative tool, ionic liquids (ILs) are widely employed as an alternative, smart, reaction media (vs. traditional solvents) offering interesting technology solutions for dissolving, processing and recycling of metal-containing materials. The costly mining and refining of rare earths (RE), combined with increasing demand for high-tech and energy-related applications around the world, urgently requires effective approaches to improve the efficiency of rare earth separation and recovery. In this context, ionic liquids appear as an attractive technology solution. This review addresses the structural and coordination chemistry of ionic liquids comprising rare earth metals with the aim to add to understanding prospects of ionic liquids in the chemistry of rare earths.

Contents

Abbreviations: ILs, ionic liquids; RE, rare earth; FCC, fluid cracking catalysts; GBCA, Gadolinium Based Contrast Agents; MRI, magnetic resonance imaging; Tf_2N^- (known also as $TFSI^-$), bis(trifluoromethanesulfonyl)amide; RTIL, room-temperature ionic liquid; C_1C_3pyr, 1-methyl-1-propylpyrrolidinium; C_1C_4pyr, 1-methyl-1-butylpyrrolidinium; OTf^-, trifluorosulfonate; C.N., coordination number; CV, cyclic voltammetry; HWP, halfwave potentials; DTSA, ditoluenesulfonylamide; DETCAP, diethyl-2,2,2-trichloroacetylphosphoramidate; C_2mim (sometimes also denoted as C_1C_2im), 1-ethyl-3-methylimidazolium; C_4mim (or C_1C_4im), 1-butyl-3-methylimidazolium; C_6mim (or C_1C_6im), 1-hexyl-3-methylimidazolium; C_{12}mim (or C_1C_{12}im), 1-dodecyl-1methyl-3-methylimidazolium; C_{14}mim (or C_1C_{14}im), 1-tetradecyl-3-methylimidazolium; C_{16}mim (or C_1C_{16}im), 1-hexadecyl-3-methylimidazolium; C_{18}mim (or C_1C_{18}im), 1-octadecyl-3-methylimidazolium; TTA, 2-thenoyltrifluoroacetonate; Hhfacac, hexafluoroacetylacetone; OPC, organic plastic crystal; $[P_{66614}]^+$, trihexyl(tetradecyl)phosphonium; $[P_{4444}]^+$, butyltetraphosphonium; $[PR_4]^+$, tetraalkylphosphonium; SXRD, single crystal X-ray diffraction; DSC, differential scanning calorimetry; MC_1mim, 1,2,3-trimethylimidazolium; dca, dicyanamide; tcm, tricyanomethanide; dcnm, dicyanonitrosomethanide; DNtM, dinitromethanide; NtCM, cyanonitromethanide; NtDCM, dicyanonitromethanide; NtNCM, cyanonitronitrosomethanide; N_{2222}, tetraethylammonium; bet^-, $Me_3N^+–CH_2COO$; cmim, N-carboxymethylimidazolium; HALO (known also as halophosphate), $(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+},Mn^{2+}$ phosphor; *dc*, direct current; PMMA, poly(methylmethacrylate).

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1. Introduction

Chemistry of the rare earths has developed rapidly during the last 30 years due to an enormous number of diverse applications [1]. The production and application of rare earth compounds constitute an important strategic and dynamic segment of the energy production, electronic and chemical industries (Fig. 1). New markets are developing for individual high-purity rare earths, particularly for neodymium and dysprosium for use in high-performance permanent magnets. A variety of motors and actuators (total number >10^8 per year) depend on permanent magnets in huge quantities and averages to more than 9.5 g of rare earth magnet per terrestrial [2].

Most people would be surprised at how extensively magnets are used in everyday life. Magnets are being utilized to help us perform certain operations when we drive cars, listen to music, work on our computer or use electrical power from wind farms. Almost 65% of the rare earths used in the U.S. and Western Europe are consumed in catalysts mainly as FCC catalysts (Fluid Catalytic Cracking) for crude petroleum refining. Contrasting with physical separation processes such as atmospheric or vacuum distillations, the FCC uses the heat and catalyst to transform larger molecules of gas oil into the smaller molecules included of distillate, gasoline butane/propane and other important products.

Coordination chelates of gadolinium – Gadolinium-Based Contrast Agents (GBCA) – are intravenous drugs which make abnormalities, specific tissues or disease processes more obviously visible on magnetic resonance imaging (MRI) examinations. Also, the worldwide need for rare earths has enormously increased due to consumer desire for light weight, compact or super-miniaturized electronic devices such as cell phones, flat panel displays and an increasing demand for ‘green’ and energy efficient technologies such as hybrid cars, wind turbines and lighting devices.

Molecular-based multifunctional materials can permit the utilization of the abundance of molecular structures to implement in technology some original and entirely surprising properties. Among the next gen transistors, sensors and memory devices, those based on spin state of molecules represent favorable substitutes to long-standing technologies. Single-molecule magnets (SMMs), single-ion magnets (SIMs) and single-chain magnets (SCMs) comprising some rare earth metals are part of the most hopeful systems for the development of novel molecular electronics based on spin transport. That kind of molecular assembly, uniting the benefits of the molecular scale with the properties of bulk magnetic materials, appears to be attractive for quantum computing and high-density information storage [3].

An unconventional route for low-temperature refrigeration can be provided by molecules with negligible magnetic anisotropy and large spin ground state which displaying a large magnetocaloric effect (MCE) [4,5]. Magnetocaloric effect is the key tool of near-room-temperature magnetic cooling with large commercialization potential in the future. Also its use is particularly attractive for very challenging conditions, such as aerospace applications [5].

Unique spectroscopic properties of lanthanide ions with attitude to the light amplification and generation provide us an access to exciting new developments in drug delivery, bioimaging, security tags, solar energy conversion, luminescent sensors and many other applications [6]. The continuous development and improvement of lanthanide-based materials for cutting-edge applications together with the fact that in majority cases rare earths are considered to be irreplaceable asks for more elaborate non-trivial and advanced synthetic approaches. One of them certainly is the use of ionic liquids (ILs) (Fig. 2).

The exploration of ionic liquids (ILs) as unique, uncommon solvents is a quickly developing area over the past few decades, also, with the focus on the decisive goal of large-scale industrial uses. These fluids can provide some properties which cannot be realized in traditional solvents. These properties include high conductivity, negligible vapor pressure at room temperature, high thermal and chemical stability over a wide temperature range, and non-flammability.

Fig. 1. Some applications of rare earths in everyday life.