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Anionic Rare-Earth Thiocyanate Complexes as Building Blocks for Low-Melting Metal-Containing Ionic Liquids

Peter Nockemann,* Ben Thijs, Niels Postelmans, Kristof Van Hecke, Luc Van Meervelt, and Koen Binnemans

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received June 8, 2006; E-mail: peter.nockemann@chem.kuleuven.be

Ionic liquids have attracted considerable attention during the past few years due to their very low vapor pressure, their wide liquidus range, their good electric conductivity, their large electrochemical window, and their potential as solvents for liquid–liquid extraction.¹ Metal-containing ionic liquids based on imidazolium salts are regarded as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic, or catalytic properties depending on the enclosed metal ion used.² However, the solubility of lanthanide complexes in ionic liquids is generally rather low. An ionic liquid containing high concentrations of lanthanides possesses potential for applications related to electrodeposition, catalysis, or photophysics. Therefore it is desirable to design lanthanide compounds that are highly soluble in ionic liquids or that are ionic liquids themselves. Some recent publications have addressed lanthanide-doped ionic liquids, which exhibit interesting luminescent properties and a good photochemical stability.³

The melting points of ionic liquids are affected by several parameters. Primarily, the size and charge delocalization of anions and cations, as well as their symmetry, play an important role, but also a poor packing- and hydrogen-bonding ability have to be taken into account.⁴ Metal-containing ionic liquids with low melting temperatures have already been reported for some mono- or divalent transition metal anions, but for a metal-containing ionic liquid with an anionic charge of -3 , a low melting point is not expected. To the best of our knowledge, no metal-containing ionic liquids with highly charged species have been described yet. Typical ligands for metalate ions are halides or thiocyanates. The classification of the thiocyanate ion as a pseudohalide emphasizes its chemical similarity to the halides in several ways, but the inorganic thiocyanate salts have much lower melting points than the corresponding halide salts, due to the different charge distribution.^{5,6} Lanthanide isothiocyanate anions, especially of the type $[\text{Ln}(\text{NCS})_6]^{3-}$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}–\text{Lu}$), have been the subject of several spectroscopic and structural studies.⁷

In this communication, we report on the first lanthanide-containing ionic liquids based on the 1-butyl-3-methylimidazolium (BMIM) cation and lanthanide thiocyanate anions of the general formula $[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]^{3-x}$ ($x = 6–8$; $y = 0–2$) (Figure 1). The compounds were synthesized by a metathesis procedure starting from stoichiometric amounts of lanthanide(III) perchlorate, ammonium thiocyanate, and a thiocyanate ionic liquid with the corresponding imidazolium cation. Most of these ionic liquids are found to be liquids or supercooled liquids at room temperature and tend to form glasses rather than crystals upon cooling (Figure 2). A few of the compounds of the type $[\text{BMIM}]_{x-3}[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]$ ($x = 6–8$; $y = 1–2$; $\text{Ln} = \text{La}, \text{Y}, \text{Nd}$) with water coordinated to the lanthanide ion crystallized at about 16°C from the molten state (see Table 1). The melting points of these crystals were determined

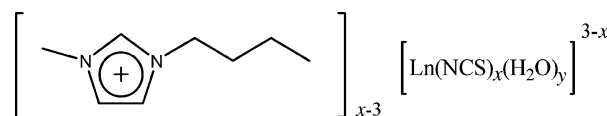


Figure 1. Structure of $[\text{BMIM}]_{x-3}[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]$ ($x = 6–8$; $y = 0–2$; $x + y < 10$; $\text{Ln} = \text{Y}, \text{La}–\text{Yb}$); BMIM = 1-butyl-3-methylimidazolium.

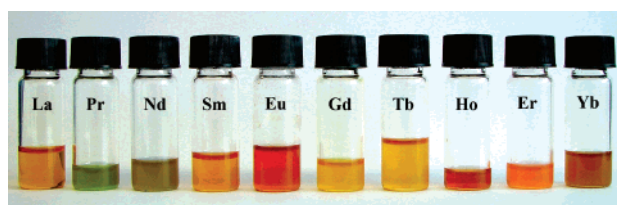


Figure 2. Ionic liquids of the type $[\text{BMIM}]_4[\text{Ln}(\text{NCS})_7(\text{H}_2\text{O})]$ with $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Er},$ and Yb . The color is due to the metalate anion.

Table 1. Characteristic Physical Data of Selected Ionic Liquids^a

compound	T_m ($^\circ\text{C}$)	T_{dec} ($^\circ\text{C}$)	ρ (g cm^{-3})	n
$[\text{BMIM}]_4[\text{Y}(\text{NCS})_6(\text{H}_2\text{O})_2]$	39	284	1.29	1.560
$[\text{BMIM}]_4[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]$	38	308	1.32	1.564
$[\text{BMIM}]_4[\text{Pr}(\text{NCS})_7(\text{H}_2\text{O})]$	33	340	1.34	1.568
$[\text{BMIM}]_4[\text{Nd}(\text{NCS})_7(\text{H}_2\text{O})]$	28	294	1.35	1.565
$[\text{BMIM}]_4[\text{Sm}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	312	1.37	1.572
$[\text{BMIM}]_4[\text{Eu}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	343	1.38	1.579
$[\text{BMIM}]_4[\text{Gd}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	332	1.44	1.580
$[\text{BMIM}]_4[\text{Tb}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	297	1.45	1.580
$[\text{BMIM}]_4[\text{Ho}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	289	1.48	1.579
$[\text{BMIM}]_4[\text{Er}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	302	1.49	1.581
$[\text{BMIM}]_4[\text{Yb}(\text{NCS})_7(\text{H}_2\text{O})]$	<rt	296	1.53	1.582
$[\text{BMIM}]_5[\text{La}(\text{NCS})_8]$	<rt	349	1.35	1.563

^a Melting point (T_m), onset of decomposition (T_{dec}), density (ρ) at 21°C , and refractive index (n); <rt = below room temperature.

by differential scanning calorimetry (DSC) and range from 28°C (Nd) to 39°C (Y).

The crystal structure of $[\text{BMIM}]_4[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]$ was determined by single-crystal X-ray diffractometry. This compound crystallized spontaneously from the molten state after standing for 5 days at 16°C . The structure shows that the lanthanum(III) ion is coordinated by seven isothiocyanate anions and one water molecule (Figure 3). The coordination number of the lanthanum(III) ion is eight, and the coordination polyhedron of the lanthanum(III) ion can be described as a slightly distorted square antiprism. Although the thiocyanate anion has an almost linear structure, the $\text{M}–\text{N}–\text{S}$ angles deviate from strict linearity and range from 157.6 to 178.2° . Each $[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]^{4-}$ moiety is surrounded by four imidazolium cations. The coordinated water molecule forms strong hydrogen bonds ($d(\text{O}–\text{H} \cdots \text{S})$ 2.48 and 2.58 \AA) to the isothiocyanate anion of the neighboring $[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]^{4-}$ unit with a $\text{C}–\text{S} \cdots \text{H}$ angle of 90.8 and 97.4° , respectively, which is in the range of reported values for hydrogen bonding.⁸ The hydrogen bonding results in a

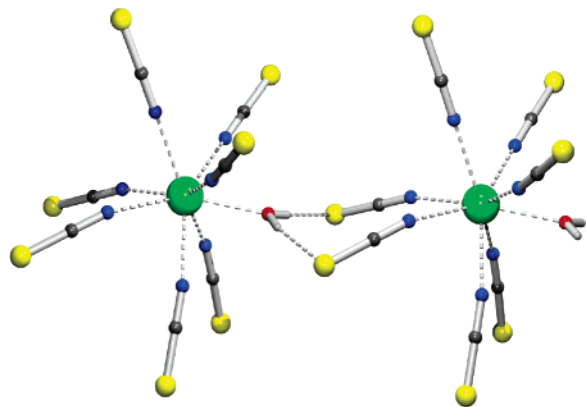


Figure 3. Molecular structure of the anionic unit $[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]^{4-}$ showing the hydrogen bonding from coordinated water molecules to the isothiocyanate anions. The $[\text{BMIM}]^+$ cations were omitted for clarity.

columnar stacking of these units along the direction of the a axis. The acidic hydrogen atoms of the imidazolium cation form weak hydrogen bonds to the sulfur of the thiocyanate anions ($\text{C}-\text{H}\cdots\text{S}$ from 2.73 up to 2.84 Å). This kind of hydrogen bonding from the imidazolium cation is in agreement with the reported $\text{C}-\text{H}\cdots\text{X}$ hydrogen bonding in imidazolium ionic liquids and metal-containing imidazolium ionic liquids.⁹ The fact that some of the ionic liquids that contain coordinated water molecules form hydrogen bonds, resulting in a polymeric stacking of the anions, might explain the better ability to crystallize. Indeed, the complexes of the type $[\text{BMIM}]_5[\text{Ln}(\text{NCS})_8]$ do not possess any $\text{O}-\text{H}\cdots\text{S}$ hydrogen bonding capability. At temperatures as low as -20°C , these compounds are not solid but are highly viscous liquids.

The lanthanide-containing compounds exhibit a complete miscibility with other imidazolium-based ionic liquids, such as $[\text{BMIM}]\text{-Cl}$, but also with hydrophobic ionic liquids, such as $[\text{BMIM}][\text{TF}_2\text{N}]$ ($\text{TF}_2\text{N} = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$) and $[\text{BMIM}][\text{PF}_6]$. Furthermore, a good solubility in apolar solvents, such as dichloromethane, was found for the compounds with seven or eight thiocyanates. In contrast, the compounds of the type $[\text{BMIM}]_3[\text{Ln}(\text{NCS})_6(\text{H}_2\text{O})_2]$ were found to be insoluble in dichloromethane. All the compounds are soluble in water, but they undergo complete hydrolysis (as proven by emission lifetime experiments).¹⁰

The absorption spectra for the crystalline state and the liquid state of $[\text{BMIM}]_4[\text{Ln}(\text{NCS})_7(\text{H}_2\text{O})]$ ($\text{Ln} = \text{Pr}, \text{Nd}$) were compared. No significant differences were observed for the ratios of the integrated intensities of the $f-f$ transitions. The trivalent neodymium ion has a hypersensitive transition $^4\text{G}_{5/2} \leftarrow ^4\text{I}_{9/2}$ (at about 586 nm) that can reflect small changes in the ligand coordination sphere.¹¹ Even the ratios of the intensity of this transition to the other transitions are very similar in the solid and liquid state. Therefore, the experimental data obtained from the absorption spectra of the ionic liquids in the solid state and in the liquid state support the hypothesis that the multicharged anionic species observed in the solid compounds persist in the liquid state.

In summary, we synthesized low-melting lanthanide-containing ionic liquids of the type $[\text{BMIM}]_{x-3}[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]$ ($x = 6-8$, $y = 0-2$, $\text{Ln} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Er}, \text{and Yb}$). The compounds are transparent liquids at room temperature. The crystal structure of $[\text{BMIM}]_4[\text{La}(\text{NCS})_7(\text{H}_2\text{O})]$ indicates that hy-

drogen bonding might influence the melting points. The compounds exhibit a good solubility in apolar solvents as well as a good miscibility with other ionic liquids, and they are therefore interesting candidates for catalytic and spectroscopic applications. Extension of the alkyl chain length of the imidazolium cation could lead to the formation of liquid-crystalline phases.¹²

Acknowledgment. Financial support by the F.W.O.-Flanders (G.0117.03) and by the K.U. Leuven (GOA 03/03 and IDO/05/005) is gratefully acknowledged. CHN analyses were made by Dirk Henot.

Supporting Information Available: Synthesis, crystallographic data of **1**, CHN, and IR and UV/vis absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0640391