Inorg. Chem. **2005**, *44*, 8168–8169

Inorganic Chemistry
Communication

Rare-Earth Iodides in Ionic Liquids: The Crystal Structure of $[SEt_3]_3[LnI_6]$ (Ln = Nd, Sm)

Arash Babai and Anja-Verena Mudring*

Insititut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

Received September 8, 2005

Crystals of $[SEt_3]_3[LnI_6]$ (Ln = Nd, Sm) were obtained by the reaction of LnI_2 with the ionic liquid $[SEt_3][Tf_2N]$ [Tf_2N = bis(trifluoromethanesulfonyl)imide]. The compounds are characterized by octahedral $[LnI_6]^{3-}$ units that are surrounded by a distorted cube of triethylsulfonium cations.

Symmetric trialkylsulfonium-based ionic liquids (ILs) have gained considerable attention as electrolytes,[1] especially with the bis(trifluoromethanesulfonyl)imide (Tf_2N^-) anion because their conductivities are among the highest found for aliphatic onium-based room-temperature ILs (RTILs).[2] Although trialkylsulfonium Tf_2N^- ILs show a large electrochemical window, the cathodic limit of decomposition is generally shifted downward compared to similar quaternary ammonium-based ILs and reaches values (in the cathodic range) that are otherwise typically found for imidazolium ILs.[2] The chemical lability of trialkylsulfonium ILs toward reduction not only influences the electrochemistry but also strongly influences the chemistry.

We are currently studying the chemistry of divalent rare-earth compounds in miscelleaneous ILs because the properties of this class of solvents can be tuned in such a way as to stabilize highly reducing species.[3] It has been well-established now that the redox potentials of divalent rare-earth cations cover a wide range and can reach values similar to those of alkali metals.[4,5] Particularly, investigations on the reactivity of SmI_2 in different ILs are of eminent interest because SmI_2, the so-called Kagan reagent, is one of the most versatile reduction reagents used in organic chemistry.[6] We were able to obtain long-time stable solutions of SmI_2 (and YbI_2) in, for example, [mppyr][Tf_2N] (mppyr = 1-methyl-1-propylpyrrolidinium).[3] In contrast, a solution of SmI_2 (as well as a solution of NdI_2) in the sulfonium-based IL $[SEt_3][Tf_2N]$ leads to the reduction of the cation of the IL. The IL decomposes to a dark-brown liquid of higher viscosity and evolves a smell reminiscent of garlic when exposed to the atmosphere.[7] To determine the product of decomposition on the side of the rare-earth cation, the respective rare-earth diiodides, LnI_2 (Ln = Nd, Sm), were reacted with $[SEt_3][Tf_2N]$ at elevated temperatures.[8] After slow cooling of the reaction mixture, room-temperature crystals of sufficient quality for single-crystal X-ray structure analysis were obtained.[9]

The structures of the isotopic compounds $[SEt_3]_3[LnI_6]$ (Ln = Nd, Sm; Figure 1) are characterized by a nearly ideal $[LnI_6]^{3-}$ octahedron. The mean interatomic distances of $d(\text{Nd}-\text{I}) = 311$ pm and $d(\text{Sm}-\text{I}) = 309$ pm are well in the expected range and reflect the radii contraction along the series of trivalent rare-earth cations.

Especially noteworthy is the second coordination sphere of the rare-earth cations. Each of the triangular faces of the $[LnI_6]^{3-}$ octahedron is capped by a triethylsulfonium cation,

---

* To whom correspondence should be addressed. E-mail: a.mudring@uni-koeln.de. Tel: +49 221 4703921. Fax: +49 221 4705083. Web page: www.anjamudring.de.

(1) Stegemann, H.; Rode, A.; Reiche, A.; Schnittke, A.; Füllbier, H. *Electrochim. Acta* **1990**, *37*, 379. Paulsson, H.; Hagfeldt, A.; Kloo, L. *J. Phys. Chem. B* **2003**, *107*, 13665. Paulsson, H.; Berggrund, M.; Vantesson, E.; Hagfeldt, A.; Kloo, L. *Sol. Energy Mater. Sol. Cells* **2004**, *82*, 345. Li, X.; Johnson, K. E. *Can. J. Chem.* **2004**, *82*, 491.

(2) Matsumoto, H.; Matsuda, T.; Miyazaki, Y. *Chem. Lett.* **2000**, 1430.

(3) Mudring, A.; Babai, A.; Arenz, S.; Giernoth, R. *Angew. Chem.* **2005**, *117*, 5621; *Angew. Chem., Int. Ed.* **2005**, *34*, 5485.

(4) Meyer, G. *Chem. Rev.* **1988**, *88*, 93.

(5) Morss, L. In *Handbook of the Physics and Chemistry of Rare Earth*; Gschneidner, K. A., Eyring, L., Choppin, G. R., Lander, G. H., Eds.; Elsevier: New York, 1994; Vol. 8, Chapter 122. Strange, P.; Svane, A.; Temmermann, W. M.; Szotek, Z.; Winter, H. *Nature* **1999**, *399*, 756.

(6) Smith, M. B., March, J., Eds. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; Wiley-Interscience: New York, 2001. Kagan, H. B. *New J. Chem.* **1990**, 14.

(7) So far we have been unable to determine the exact identity of the decomposition products, which apparently are of a complex nature. Reduction of the triethylsulfonium cation apparently leads to cleavage of the S−C bond and subsequent polymerization. When exposed to the atmosphere, hydrolysis takes place and sulfanes are formed.

(8) Experimental information: $[SEt_3][[Tf_2N]$ was prepared according to the literature procedure.[2] LnI_2 (Ln = Sm, Nd) was prepared by the reduction of LnI_3 with the corresponding Ln metal in a sealed tantalum container, jacketed with an evacuated silica tube. LnI_3 was prepared from metal (chips, Chempur, 99.5%) and iodine (Riedel de Häen, 99.8%) according to the procedure described in the literature.[13] Storage and manipulation of the starting materials and products were handled under drybox conditions (MBraun, Garching, Germany). The reaction of LnI_2 (0.22 mmol, ~88 mg) with $[SEt_3][Tf_2N]$ (1.8 mmol, 0.73 g, 0.5 mL) was carried out in an evacuated and sealed silica tube at 393 K for 12 h. Yellow (Sm) and pale-green (Nd) single crystals of $[SEt_3]_3[LnI_6]$ formed as an insoluble product after subsequent cooling (2 K/min) to room temperature. The product was separated by filtration. Estimated yields: ~15%.

10.1021/ic051533h CCC: $30.25

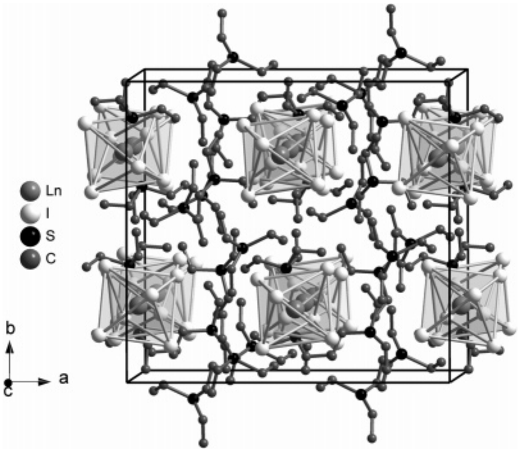

Figure 1. Crystal structure of $[SEt_3]_3[LnI_6]$. Hydrogen atoms and disorder in the SEt_3^+ part of the structure are omitted for clarity.

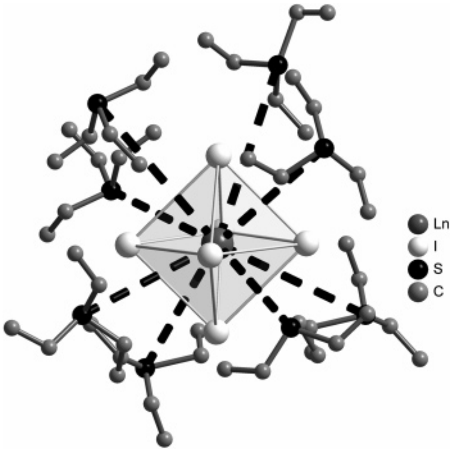

Figure 2. First and second coordination sphere of Ln^{3+} in $[SEt_3]_3[LnI_6]$. Hydrogen atoms and disorder in the SEt_3^+ structure part are omitted for clarity.

leading to the formation of a (distorted) cube (Figure 2). This structural feature has already been predicted by molecular dynamic studies to occur for $[LnCl_6]^{3-}$ in imidazolium ILs[10] and has been observed in compounds obtained from the IL [mppyr][Tf_2N].[11] A similar structural motif has recently been found for $[PF_6]^-$ in the IL [dmim][PF_6] (dmim = 1,3-dimethylimidazolium).[12] Therefrom, the general conclusion can be drawn that for anionic octahedral units such as $[MX_6]^{x-}$ a second coordination sphere of a cube of cations (of the IL) is a common structural feature.

The high conformational flexiblity of the triethylsulfonium cation, which, on the one hand, is a prerequisite for a cation of an IL, becomes a crucial problem when trying to get crystals of sufficient quality for X-ray structure analysis. As has already been noted for the Tf_2N^- anion,[3] conformational flexiblity and a well-shielded or delocalized charge often lead to strong disorder in the crystal. However, in the case of $[SEt_3]_3[NdI_6]$, we were able to obtain high-quality crystals, which allowed not only positioning of the cations but also their anisotropic refinement and even refinement of hydrogen positions after the riding model. Thus, the structure of the triethylsulfonium cation could be determined reliably. Awareness has to be drawn to the fact that the cation is far from being planar, as has been mentioned occasionally in the literature,[1,2] but shows a strong tetrahedralization at the central sulfur atom with C−S−C bonding angles of about 101°.

Acknowledgment. A.-V.M. thanks the Deutsche Forschungsgemeinschaft (Grant SPP 1166, “Lanthanoidspezifische Funktionalitäten”) and the Fonds der Chemischen Industrie (supplies and Liebig fellowship) for their support as well as Prof. Dr. G. Meyer for his interest in our ongoing research.

Supporting Information Available: Further crystallographic information are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051533H

---

(9) Crystal data: Suitable single crystals were mounted under inert conditions in glass capillaries. Intensity data sets were collected on an IPDS II diffractometer (Stoe, Darmstadt, Germany). The crystal structures were solved by direct methods (SIR-92; Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343). Subsequent difference Fourier analyses revealed the remaining atom positions. The structures were refined with SHELXL-97 (Sheldrick, G. M., Institut für Anorganische Chemie der Universität, Tammanstrasse 4, Göttingen, Germany, 1998). Numerical absorption correction after crystal shape optimization was performed using the programs X-Red 1.01 and X-Shape 1.01 (Stoe, Darmstadt, Germany). $[SEt_3]_3[NdI_6]$: $S_3C_9H_{45}NdI_6$, $M = 1251.3$, orthorhombic, $a = 1942.6(2)$ pm, $b = 1816.3(3)$ pm, $c = 2143.5(4)$ pm, $U = 7563.1(2)$ Å, $T = 298$ K, space group *Pbca* (No. 61), $Z = 8$, $\mu(\mathrm{Mo\ K\alpha}) = 6.442\ \mathrm{mm}^{-1}$, 71 340 reflections measured, 8902 unique ($R_{int} = 0.404$), which were used in all calculations. The final R1 was 0.093, and the final wR2 was 0.159 (observed data). $[SEt_3]_3[SmI_6]$: $S_3C_9H_{45}SmI_6$, $M = 1257.4$, orthorhombic, $a = 1936.8(1)$ pm, $b = 1807.07(7)$ pm, $c = 2116.47(8)$ pm, $U = 7407.47(6)$ Å, $T = 170$ K, space group *Pbca* (No. 61), $Z = 8$, $\mu(\mathrm{Mo\ K\alpha}) = 6.761\ \mathrm{mm}^{-1}$, 79 255 reflections measured, 8117 unique ($R_{int} = 0.101$), which were used in all calculations. The final R1 was 0.051, and the final wR2 was 0.076 (observed data). Hydrogen positions were treated with the “riding model”, and disorder was taken into account.

(10) Chaumont, A.; Wipff, G. *J. Phys. Chem. B* **2004**, *108*, 3311.

(11) Babai, A.; Mudring, A.-V. *J. Alloys Compd.* **2005**, in press.

(12) Hardacre, Ch.; McMath, S. E. J.; Niewenhuyzen, M.; Bowron, D. T.; Soper, A. K. *J. Phys.: Condens. Matter* **2003**, *15*, 159.

(13) Corbett, J. D. *Inorg. Synth.* **1983**, *22*, 31. Meyer, G. In *Synthesis of Lanthanide and Actinide Compounds*; Meyer, G., Morss, L., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; pp 135−144.