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Novel electrosynthesis of metallic bis(trifluoromethanesulfonyl) imides

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Abstract—The preparation of a series of bis(trifluoromethanesulfonyl) imide salts of various metals was effected in good yields, under clean, mild and anhydrous conditions, by using a simple electrochemical methodology. © 2003 Elsevier Science Ltd. All rights reserved.

Bis(trifluoromethanesulfonyl) imide or $(CF_3SO_2)_2NH$, commonly known as TFSI, is a strong acid whose pK_a in water has been evaluated to 1.7.[1] The corresponding bis(trifluoromethanesulfonyl) imide salts have shown strong Lewis acid character, in particular in alkylation,[2] acylation,[3,4] nucleophilic substitution[5] and Diels–Alder reactions.[6,7] However, only the lithium salt has known an important industrial development for its applications as electrolyte in batteries for electric vehicles.[8–10] Except for the lithium salt, other metallic bis(trifluoromethanesulfonyl) imide salts are not commercially available.

The preparation of metal salts of bis(trifluoromethanesulfonyl) imide is generally carried out from the corresponding metal oxides,[3] hydroxides[5] or carbonates[11] in the presence of TFSI. The reactions are generally carried out in an aqueous medium, necessary to dissolve the starting metallic derivatives. The corresponding bis(trifluoromethanesulfonyl) imide salts, generally obtained in good yields, are thus fully hydrated and decompose before their complete dehydration.

We present here, as an alternative, a very simple electrochemical procedure for the direct, mild, clean and efficient preparation of metallic bis(trifluoromethanesulfonyl) imide salts under anhydrous conditions. To our knowledge, no electrochemical synthesis of these salts has been yet reported. The electrochemical methodology has already been used for the preparation of, for example, metal carboxylates,[12,13] or alkoxides,[14] as well as of some organometallic complexes.[15,16]

The electrochemical method for the preparation of metallic bis(trifluoromethanesulfonyl) imide salts is based on the use of one-compartment cells[17,18] in which the sacrificial anode is constituted by a rod of the metal to be oxidised. The cathode is inert, constituted of carbon fibre or stainless steel. A TFSI solution in a polar organic solvent such as DMF or nitromethane is electrolysed at room temperature under constant current intensity, without the need of added supporting electrolyte. The reactions at the electrodes are, at the cathode, the reduction of the acid to form the bis(trifluoromethanesulfonyl) imide anion and dihydrogen, which is evolved, and at the anode, the oxidation of the metal rod to the corresponding cations. In solution, the formation of the metallic bis(trifluoromethanesulfonyl) imide salts occurs, according to Scheme 1.

The reaction is carried out smoothly, at room temperature and it is stopped after the passage of 1 F/mol of acid. The only by-product of the synthesis is dihydrogen. After solvent evaporation, the non-hydrated salts are obtained in good yields, though coordinated to some solvent molecules.

Cathodic reaction: $(Tf)_2NH + e^- \longrightarrow (Tf)_2N^- + 1/2\, H_2$

Anodic reaction: $M \longrightarrow M^{+n} + n\, e^-$

In solution: $(Tf)_2NH + M \longrightarrow M^{+n}\, [(Tf)_2N^-]_n + 1/2\, H_2$

Scheme 1. Reactions at the electrodes.

Keywords: electrochemical; bis(trifluoromethanesulfonyl) imide salts; Lewis acids; sacrificial metal anode; TFSI.

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Table 1. Electrochemical synthesis of metallic bis(trifluoromethanesulfonyl) imide salts

Metal (anode)	Solvent	Cathode	Yield (%)	$M(NTf_2)_n$ obtained
Mg	DMF	Stainless steel	95	$Mg(NTf_2)_2 \cdot 5–6DMF$
Mg	CH_3NO_2	Stainless steel	98	$Mg(NTf_2)_2 \cdot 0.1MeNO_2$
Sm	DMF	C fiber	95	$Sm(NTf_2)_3 \cdot 7–8DMF$
Al	CH_3NO_2	Stainless steel	92	$Al(NTf_2)_3 \cdot 1.4MeNO_2$
V	CH_3NO_2	C fiber	93	$V(NTf_2)_2 \cdot 0.7MeNO_2$
Zn	DMF	C fiber	78	$Zn(NTf_2)_2 \cdot 6DMF$
Ni	DMF	Stainless steel	98	$Ni(NTf_2)_2 \cdot 6DMF$

Almost quantitative yields of different metal salts were obtained, as summarised in Table 1. The salts prepared were reasonably soluble in chloroform, DMF, DMSO and acetonitrile. ^{19}F and ^1H NMR were recorded in $CDCl_3$ or DMSO-d_6 with 1-chloro-4-trifluoromethylbenzene as a standard, to enable quantification of solvent protons relative to CF_3 groups.

Combination of NMR and elemental analysis allowed to propose the molecular structures for the series of these new salts. A very small variation of the ^{19}F NMR signal of the CF_3 groups of the different salts could be observed. Whereas the CF_3 groups appeared at −75.55 ppm for TFSI in $CDCl_3$ (reference: p-$ClC_6H_4CF_3$ at −63.0 ppm), they were shifted to −79.40, −79.54 and −79.96 ppm for the Zn^{2+}, Mg^{2+} and V^{2+} salts, respectively. In DMSO-d_6, the CF_3 groups for TFSI appeared at −80.52 ppm, and the Sm^{3+}, Al^{3+} and Ni^{2+} salts appeared very close, all located from −80.51 to −80.59 ppm.

The influence of the solvent was not determinant for the yields of the reaction, as could be observed by comparing the preparation of $Mg(NTf)_2$ in DMF or in nitromethane. However, the choice of the reaction solvent was important: THF underwent polymerisation and diethyl ether and alcohols were decomposed by TFSI. Nitromethane and DMF could be used efficiently within the range of metals tested. Is was observed that salt preparations run in DMF led to complexes with 5–8 solvent molecules, whereas with nitromethane only 0.1–1.4 molecules of this low coordinating solvent were found in the corresponding salts.

In conclusion, we present here a novel and alternative procedure for the efficient and clean preparation of metallic bis(trifluoromethanesulfonyl) imide salts under anhydrous conditions. These compounds present promising perspectives as catalysts in organic chemistry, due to their expected high Lewis acidity, the high dissociation character of the anion and their enhanced solubility in organic solvents.

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