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Antimony(V) and Tin(IV) Complexes with Redox-Active O,N,O-Donor Ligand in the Electrosynthesis of Symmetrical Disulfides

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Abstract—Reactions of electrochemically generated antimony(V) and tin(IV) complex species containing a tridentate O,N,O-donor ligand with various thiols were studied. Among main group metal complexes with *N*,*N*-bis(2-hydroxy-di-3,5-*tert*-butylphenyl)amine ($CatH_2$–NH–$CatH_2$), compounds [Me_2Sn(Cat-N-SQ)] (**I**), [Et_2Sn(Cat-N-SQ)] (**II**), [Ph_2Sn(Cat-N-SQ)] (**III**), [$(c\text{-}C_6H_{11})_2Sb$(Cat-N-Cat)] (**IV**), and [Ph_3Sb(Cat-NH-Cat)] (**V**) are the most active, able to mediate the oxidation of thiols (1-hexanethiol, cyclohexanethiol, and 4-methoxythiophenol), to symmetrical disulfides were identified. The anodic activation of Sb(V) and Sn(IV) complexes involves organic ligands and gives rise to intermediates that react with thiols. During the mediated electrosynthesis, the initial complex species is regenerated in solution. The use of metal complex mediators decreases the anodic overvoltage of the thiol oxidation in comparison with direct electrochemical synthesis. The yields of products depend on complex and thiol structures or ratio. The highest efficiency in the electrocatalytic reactions was found for the [Ph_3Sb(Cat-NH-Cat)] complex, which should be used for the synthesis of disulfides.

Keywords: antimony(V) and tin(IV) complexes, redox-active ligands, redox mediators, thiols, symmetrical disulfides, anodic activation, electrosynthesis

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INTRODUCTION

Organic redox-active ligands coordinated to a transition or main group metal ion attract considerable attention in the organometallic chemistry. Metal complexes of this type exhibit specific properties: redox isomerism, various types of magnetic exchange interactions, and redox transitions in the ligand environment. Ligands with variable oxidation state are used as reservoirs for electron storage/transfer in chemical reactions or for bond formation or cleavage [1–4]. The coordination of redox-active ligands to the metal center offers new opportunities for conducting reactions that require several redox equivalents or transfer of atoms or functional groups.

The ability of redox-active ligands to change the oxidation state within the metal coordination sphere is the particular interest for the chemistry of main group metal derivatives. This is due to the fact that these metals usually can not exist in many oxidation states. The presence of redox-active ligands in the coordination sphere of a main group element markedly expands the scope of reactivity of complexes due to participation of organic groups in electron transfer reactions [5, 6]. Metal complexes are rather efficiently used in organic electrosynthesis as oxidants/reductants or mediators [7]. This approach, based on green chemistry principles, reduces energy expenditure and adverse impact on the environment and may solve some environment problems [8]. The advantages of mediated electrosynthesis include mild reaction conditions (25°C, 1 atm), high selectivity to the target reaction pathway, cyclicity of electrode processes, and lower overvoltage in comparison with direct electrosynthesis [9].

Previously, we demonstrated the efficiency of using of transition metals (chromium(III), nickel(II), indium(III)), with bidentate O,O- and S,S-ligands as mediators of H_2S oxidation for the thiolation of cycloalkanes, alkenes, and arenes [9–11].

There are known examples of using organic and inorganic mediators in the oxidation of thiols to disulfides in polar solvents at room temperature [12–15]. The synthesis of disulfides is demanded as these compounds are used in the production of pesticides, oil additives, odorants, fragrances, and drugs (anti-inflammatory, antineoplastic, and anti-allergic) [16]. Main group metal complexes with redox-active ligands have not been considered previously as electromediators of thiol oxidation. However, the electrochemical properties of antimony(V) and tin(IV) complexes with tridentate O,N,O-donor ligand existing in different oxidation states imply the possibility of generating stable redox forms [17, 18]. Good prospects of using complexes with ligands of this type are sup-

Table 1. Data of mass spectrometric analysis for synthesized disulfides and starting thiols

Compound	m/z (I, %)
$C_6H_{13}SH$	118 $[M]^+$ (31), 84 (12), 69 (33), 56 (100), 47 (18), 41 (48)
$(C_6H_{13}S)_2$	234 $[M]^+$ (10), 208 (5), 192 (5), 150 (13), 117 (15), 85 (26), 69 (10), 43 (100)
$C_6H_{11}SH$	116 $[M]^+$ (25), 83 (23), 67 (40), 55 (100), 43 (20)
$(C_6H_{11}S)_2$	230 $[M]^+$ (14), 147 (16), 83 (100), 55 (27)
4-MeOPhSH	140 $[M]^+$ (100), 125 (79), 97 (46), 77 (5), 69 (16), 53 (16), 45 (15)
$(4\text{-MeOPhS})_2$	278 $[M]^+$ (31), 139 (100), 124 (15), 96 (25), 70 (14), 45 (5)

ported by the catalytic activity of these complexes in trifluoromethylation reactions [19, 20].

This study is concerned with new mediators (Med) based on antimony(V) and tin(IV) complexes with *N*,*N*-bis(2-hydroxy-di-3,5-*tert*-butylphenyl)amine ($CatH_2$–NH–$CatH_2$) ligand in the oxidation of various thiols to symmetrical disulfides: [Me_2Sn(Cat-N-SQ)] (**I**), [Et_2Sn(Cat-N-SQ)] (**II**), [Ph_2Sn(Cat-N-SQ)] (**III**), [(c-$C_6H_{11})_2Sb$(Cat-N-Cat)] (**IV**), and [Ph_3Sb(Cat-NH-Cat)] (**V**).

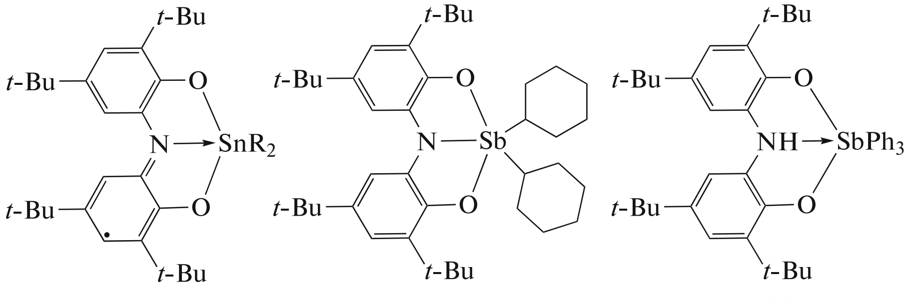
EXPERIMENTAL

Antimony(V) and tin(IV) complexes **I**–**V** were synthesized by known procedures [17, 18, 21]. Commercially available 1-hexanethiol (98%, Aldrich), cyclohexanethiol (97%, Alfa Aesar), 4-methoxythiophenol (97%, Aldrich), and hexane (reagent grade) were used as received. Reagent grade dichloromethane was purified by a known procedure [22] and then dehydrated over CaH_2. Electrochemical measurements were carried out on a IPC-Pro potentiostat with a Pt anode (d = 2 mm) in CH_2Cl_2 in the presence of 0.1 M n-Bu_4NClO_4 (+99%) pre-dried in vacuum for 48 h at 50°C. A saturated silver chloride (Ag/AgCl/KCl) reference electrode with a water-tight diaphragm was used. The electrolysis of the thiol/complex mixture was carried out on a platinum anode ($S = 70$ mm^2) in an undivided cell in dichloromethane using a PI-50.1 potentiostat and the constant potential mode. Prior to electrolysis, the solution was deaerated by purging with argon (5 min). The mediated electrosynthesis of disulfides was conducted at a more positive potential (by 0.2 V) than the oxidation potential of the mediator: 0.63–0.85 V (**I**–**IV**) and 1.20 V (**V**). The working concentration of the complexes was 0.001 mol/L. The thiol/complex ratio was 1 : 1 or 2 : 1. The time of electrolysis varied from 1.5 to 3.0 h.

After electrolysis, the disulfide was isolated by a stepwise procedure: the reaction mixture was concentrated; the supporting electrolyte was precipitated with hexane; sulfur compounds and the complexes were separated by column chromatography (silica gel as the adsorbent; elution with a 1 : 1 ethyl acetate–hexane mixture). The solution of the reaction products and unreacted thiols was subjected to electrochemical analysis (cyclic voltammetry (CV)). The current yields of the disulfides were estimated from the CV data. The products were identified by gas chromatography/mass spectrometry on a GCMS-QP2010 Ultra Shimadzu spectrometer with a combined flame photometric detector. Helium was used as the carrier gas; a SPB-1 SULFUR capillary column (30 m × 0.32 mm) was used, and silica gel served as the adsorbent, T_{max} = 320°C. The results of GC/MS analysis of sulfur compounds are summarized in Table 1.

RESULTS AND DISCUSSION

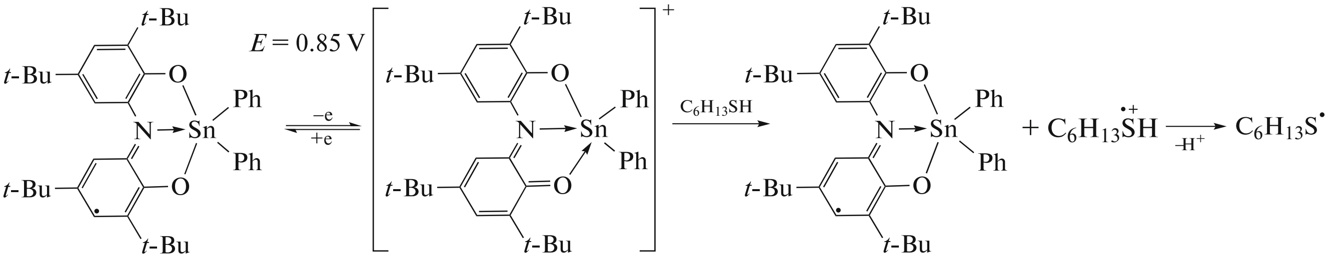
The reactions of antimony(V) and tin(IV) complexes, [Me_2Sn(Cat-N-SQ)] (**I**), [Et_2Sn(Cat-N-SQ)] (**II**), [Ph_2Sn(Cat-N-SQ)] (**III**), [(c-$C_6H_{11})_2Sb$(Cat-N-Cat)] (**IV**), and [Ph_3Sb(Cat-NH-Cat)] (**V**) (Scheme 1), with thiols under anodic activation conditions were considered.



R = Me (**I**); Et (**II**); Ph (**III**) (**IV**) (**V**)

Scheme 1.

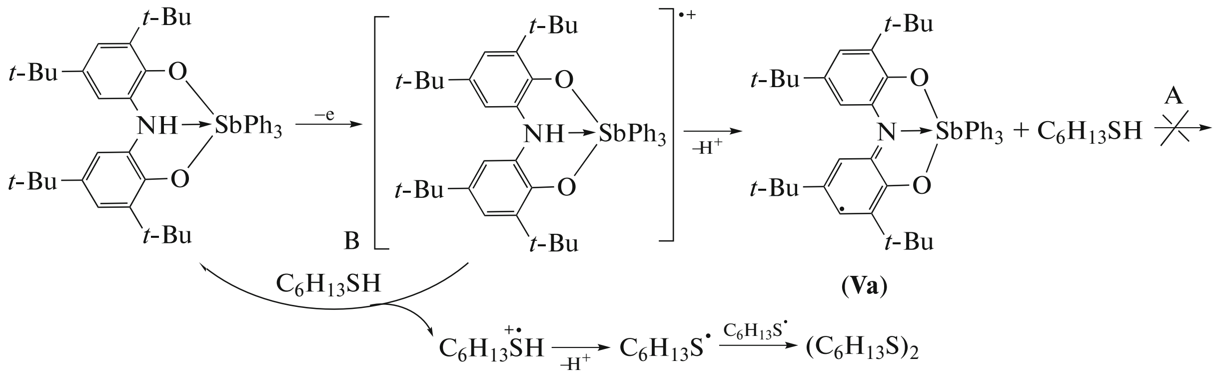
Complexes **I**–**V** differ in the oxidation state of the ligand, which exists in doubly reduced paramagnetic (Cat–N–SQ), trianionic (Cat–N–Cat), and dianionic (Cat–NH–Cat) forms. When the ligand is coordinated to a metal, the ligand redox states can be interconverted via electron and proton transfer. The electrochemical properties of the complexes were studied by CV on a platinum electrode. The anode potentials of compounds **I**–**V** correlate with the previously published values obtained using a GC electrode [18]. Complexes **I**–**III** tend to undergo two-step oxidation in the anodic region: the first quasi-reversible peak occurs in the 0.43–0.65 V potential range and corresponds to the generation of monocationic complex containing the monoanionic form of the ligand, while the second (irreversible) peak attests to a more extensive oxidation of the ligand. The reactions of compounds **I**–**III** with hexane-1-thiol without electrical activation do not result in the formation of disulfides. However, controlled potential electrolysis (0.63–0.85 V) gives the monocationic complex, which reacts with thiol in solution to give dihexyl disulfide and to regenerate the mediator (Scheme 2).



Scheme 2.

Among tin(IV) compounds, the highest efficiency was found for complex **III** with phenyl groups at the metal, which is due to the higher stability of its oxidized form. This was confirmed by CV data, in particular, reversibility ratios (I_c/I_a = 0.67 (**I**), 0.72 (**II**), 0.81(**III**)) for the first anodic step.

In the case of complex **IV**, the CV curve showed two quasi-reversible oxidation steps, resulting in the mono- and dicationic complex species (E^1_{pa} = 0.58 V; E^2_{pa} = 1.10 V). Electrolysis of compound **IV** in the presence of 1-hexanethiol did not give the expected disulfide, irrespective of the applied potential. This is attributable to the decrease in the mediator concentretion during electrolysis, which is due to the possibility of Sb–C bond cleavage in the organometallic moiety. The CV curve of compound **V** showed one irreversible oxidation peak, corresponding to the generation of reactive radical cation in the near-electrode area. As shown previously [18], the electrochemical oxidation of complex **V** affords a paramagnetic intermediate containing the dianionic paramagnetic form of the ligand. In order to establish the mechanism of reaction of compound **V** with 1-hexanethiol, we first generated the monocationic complex. The addition of the thiol did not result in the reduction of complexes oxidized form to the initial state and disulfide formation (Scheme 3, A).



Scheme 3.

Unlike this reaction pathway, the controlled potential (1.2 V) electrolysis of a mixture of complex **V** with 1-hexanethiol (1 : 1) gave $(C_6H_{13}S)_2$ (Scheme 3, B). This fact was confirmed by the CV data: the initial voltammogram exhibited two anodic peaks corresponding to the starting complex and hexane-1-thiol at a

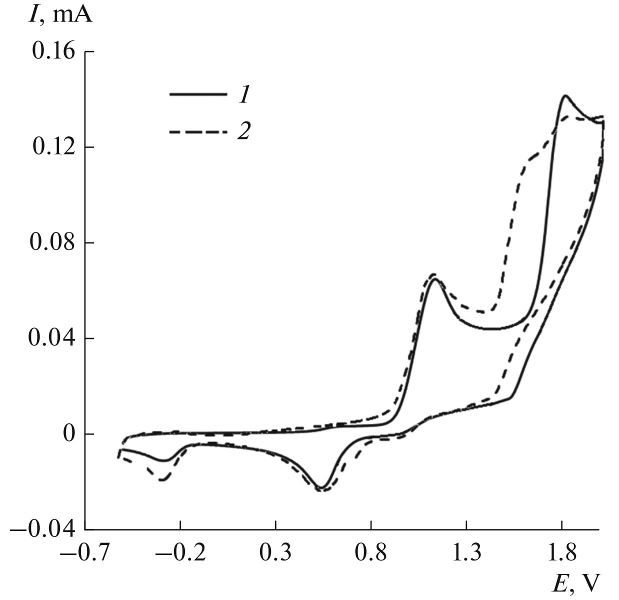


Fig. 1. CV curves for the oxidation: (curve *1*) an equimolar mixture of complex **V** with hexane-1-thiol; (curve *2*) after electrolysis at 1.20 V (1.5 h) (CH_2Cl_2, Pt anode, 0.1 M of n-Bu_4NClO_4, $c(V) = c(C_6H_{13}SH) = 0.005$ mol/L, Ag/AgCl/KCl, argon).

potential of 1.80 V (Fig. 1, *1*). After electrolysis, the intensity of the thiol oxidation peak decreased, and a new peak for the reaction product, dihexyl disulfide, appeared at 1.58 V (Fig. 1, *2*). The obtained CV curves of complex **V** before and after electrolysis attest to the stability of this complex.

Hence, compounds **III** and **V** can be used as redox mediators of oxidation of thiols to disulfides, taking into account the differences between their anodic potentials. Using **III** and **V**, mediated electrosynthesis of disulfides based on hexane-1-thiol, cyclohexane-1-thiol, and 4-methoxythiophenol was carried out under constant voltage conditions (E_{el} = 0.85 (**III**), 1.20 V (**V**), (E_{el} is the potential of electrolysis). The electrolysis gave the corresponding symmetrical disulfides, with their current yields being 47–68% (Table 2).

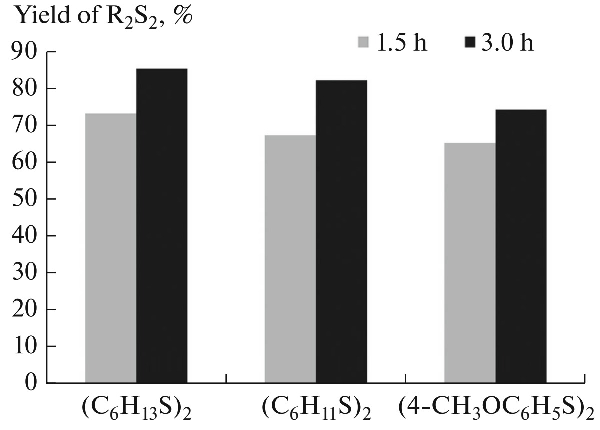


Fig. 2. Diagram of the current yields of various disulfides vs. time of mediated electrosynthesis in the presence of complex **V** (c_{Med} = 0.001 mol/L, Med : thiol = 1 : 2).

The yields of the reaction products obtained with complex **V** were higher than those in the case of complex **III**. A similar trend can be followed for the degree of conversion of thiols to disulfides. Analysis of the anodic overvoltage values in the presence of mediators attests to lower energy expenditure for the electrosynthesis compared with that in the direct anodic activation of thiols. Despite the fact that the yields of disulfides upon electrolysis (1.5 h) at the thiol oxidation potential (1.90 V) reach higher values (75–79%), the efficiency of the mediated synthesis is due to a decrease in electricity consumption. The degree of regeneration of complexes **III** and **V** was 93–95% for all of the reactions. The anodic overvoltage (ΔE) in the electrosynthesis involving complex **V** was optimal, because the values required for redox mediators were closer (Table 2) than those for complex **III** [23].

Table 2. Yield of symmetrical disulfides, conversion of thiols, and anodic overvoltage of the electrosynthesis (ΔE) using complexes **III** and **V***

Compound	Yield of R_2S_2, %	Conversion of RSH, %	ΔE, V
1-Hexanethiol	59/68**	60/72	1.05/0.71
Cyclohexanethiol	57/60	62/71	0.86/0.53
4-Methoxythiophenol	47/63	59/69	1.00/0.65

* Med : thiol = 1 : 1 (τ = 1.5 h, CH_2Cl_2, 0.1 M $n$$Bu_4NClO_4$, Pt anode ($S$ = 70 mm^2), c_{Med} = 0.001 mol/L, argon).
** The yields, conversions, and ΔE separated by a slash were obtained in the presence of complexes **III** or **V**, respectively.

Then we studied the effect of increasing content of thiol relative to mediator concentration (2 : 1) at different time of the electrosynthesis (Fig. 2).

During the reaction (1.5 h), the yield of disulfide somewhat increased in contrast to one at the equimolar mediator to thiol ratio, which is due to the absence of pronounced catalytic effect. The results on the yields of symmetrical disulfides indicate a higher reactivity of the aliphatic thiol compared with cyclohexanethiol and 4-methoxythiophenol. Doubling of the time of electrolysis did not bring about a proportional increase in the yield of disulfides, which is due to adsorption of disulfides on the platinum anode, resulting in a decrease in the number of Med regeneration cycles on the electrode. Therefore, with these reaction conditions, it is inappropriate to generate an excess of thiol with respect to the complex. An increase in the time of electrosynthesis to 3 h led to a minor decrease (86–91%) in the degree of regeneration of complex **V**. The use of main group metal complexes as the electron transfer mediators in the reactions of thiols demonstrated that the ability of the ligand to exist in different redox states increases the reactivity of compounds of this type. Note that the initial complexes and the electrochemically generated complex species remain stable and do not decompose in the presence of thiols, even though their content and duration of electrosynthesis are increased. Unlike direct electrosynthesis of symmetrical disulfides from thiols, the use of redox mediators has a number of benefits. The reaction proceeds in solution; therefore, the probability of thiol adsorption on the electrode decreases. In addition, it is possible to vary the applied electrode potential depending on the type of selected mediator: organic, inorganic, or metal complex [24]. Redox mediators are capable of being repeatedly regenerated in solution; hence, they can be used many times for the synthesis of disulfides, unlike single-electron oxidants: *o*-benzoquinones or *o*-iminobenzoquinones [25].

Thus, in this study, we proposed for the first time using complexes of main group metals, antimony(V) and tin(IV), with a tridentate O,N,O-donor ligand as electromediators of the oxidation of (cyclo)alkane- and arenethiols to symmetrical disulfides. The use of these mediators made it possible to decrease the anodic overvoltage of the electrode process by 0.53–1.05 V in comparison with the direct anodic activation of thiols. The potential range varies depending on the redox form of the coordinated ligand and on the electrochemical properties of the thiol. A higher activity in the mediated electrosynthesis of disulfides was found for Sn(IV) and Sb(V) complexes containing phenyl groups at the metal atom. The highest yield of disulfide derived from 1-hexanethiol (84%) was obtained for antimony complexes. The use of main group metal complexes with redox-active ligands as mediators of thiol oxidation was found to be expedient because of the higher energy efficiency of this environmentally safe method in comparison with the direct electrosynthesis of disulfides.

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CONFLICT OF INTEREST

The authors declare that there is no conflicts of interest.

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