ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 9, pp. 578–582. © Pleiades Publishing, Ltd., 2017.
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Chromium(III) and Indium(III) 3,6-Di-*tert*-Butyl-*o*-Semiquinolate Complexes as Redox Mediators of Hydrogen Sulfide Oxidation in Reactions with Cycloalkanes

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Received April 3, 2017

Abstract—The electrochemical oxidation of the chromium(III) and indium(III) complexes with 3,6-di-*tert*-butyl-*o*-semiquinolate leading to the formation of active monocationic species is studied by cyclic voltammetry. The reactions of the latter with hydrogen sulfide generate the radical cation of H_2S, whose fragmentation affords the proton and thiyl radical. These complexes are proposed for the first time as redox mediators for the one-pot thiolation of inert cycloalkanes C_6–C_8, which decreases the activation energy of hydrogen sulfide compared to that for direct electrochemical oxidation. The major products of cycloalkane functionalization involving H_2S are thiols and organic di- and trisulfides. The yield of the synthesized compounds depends on the type of the mediator: the chromium(III) complex exhibits the highest efficiency in the electrocatalytic transformations.

Keywords: *o*-semiquinone complexes of chromium(III) and indium(III), hydrogen sulfide, electrochemical activation, redox mediators, cyclic voltammetry

DOI: 10.1134/S107032841707003X

INTRODUCTION

In the recent time, the application of electrochemically generated catalysts gains increasing significance for organic synthesis and investigations of the mechanism of reactions of electron transfer, bond cleavage, substitution, addition, and other [1–3]. There are examples of using the metal complexes with redox-active ligands as catalysts of the chemical reactions [4]. The involvement of the metal complexes in the mediatory processes is of special interest [5]. Transition metal complexes with organic ligands can be considered as electromediators due to their redox activity. The reactions of the coordination compounds of transition metals with small molecules, such as molecular nitrogen, hydrogen, oxygen, carbon dioxide, white phosphorus, and hydrogen sulfide, are fairly well studied [6–8]. A large body of experimental material was accumulated on the use of the complexes and salts of metals in high oxidation states for the reactions involving electromediatory systems to occur: oxidation of alcohols and esters, dehydroxylation of olefins, and oxidation of arenes to quinones [9, 10].

We have previously shown the efficiency of using the chromium(III) and nickel(II) complexes with the O,O- and S,S-coordinated ligands as mediators of H_2S oxidation [11]. This work is devoted to the study of the redox properties of new mediators of hydrogen sulfide oxidation based on the chromium(III) and indium(III) complexes and their use for the SH-functionalization of inert cycloalkanes C_6–C_8.

EXPERIMENTAL

The chromium(III) and indium(III) complexes and 3,6-di-*tert*-butyl-*o*-benzoquinone were synthesized using known procedures [12, 13] at the Laboratory of Chemistry of Organoelement Compounds of the Razuvaev Institute of Organometallic Chemistry (Russian Academy of Sciences). Commercially available cycloalkanes (98%, Aldrich) and hexane (95%, Alfa Aesar) were used as received. Dichloromethane (reagent grade) was purified using a known procedure [14]. Electrochemical measurements were carried out with an IPC-Pro potentiostat at the Pt anode in CH_2Cl_2 in the presence of 0.1 M n-Bu_4NClO_4 (+99%, electrochemical grade) preliminarily dried in vacuo for 48 h at 50°C. A saturated silver chloride (Ag/AgCl/KCl) electrode with a waterproof membrane served as a reference electrode. Hydrogen sulfide was prepared using a described procedure [15].

Table 1. Redox potentials of the chromium(III) and indium(III) complexes and the redox pair 3,6-di-*tert*-butylpyrocatechol/3,6-di-*tert*-butyl-*o*-benzoquinone according to the CV data*

Compound	$E_{1/2}^{3-/2-}$, V	$E_{1/2}^{2-/1-}$, V	$E_{1/2}^{1-/0}$, V	$E_{1/2}^{0/1+}$, V	$E_{p}^{1+/2+}$, V	$E_{p}^{2+/3+}$, V
$Cr(3,6\text{-}SQ)_3$**	−1.32	−0.86	−0.24	1.02	1.24	1.54
$In(3,6\text{-}SQ)_3$	−0.94	−0.51	−0.11	0.96	1.37	
$3,6\text{-}QH_2/3,6\text{-}Q$			−0.48	1.30		

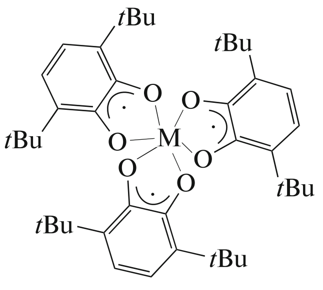
* Glassy carbon electrode, CH_2Cl_2, $V = 0.2$ V/s, 0.15 M $n\text{-}Bu_4NClO_4$, $c = 3 \times 10^{-3}$ mol/L, Ar, against Ag/AgCl/KCl (saturated); $E_{1/2}$ is the potential of the oxidation/reduction half-wave, E_p is the potential of the oxidation peak.
** The data presented are taken from [11].

The microelectrolysis of a mixture (H_2S + cycloalkane) was carried out using a PI-50.1 potentiostat in the potentiostatic regime at the potentials by 0.1 V more positive than the potential of mediatory oxidation: 1.02 V ($Cr(3,6\text{-}SQ)_3$), 0.96 V ($In(3,6\text{-}SQ)_3$), and 1.30 V ($3,6\text{-}QH_2/3,6\text{-}Q$). The working concentration of the mediators was 0.01 mol/L. The hydrogen sulfide to cycloalkane molar ratio was 1 : 5. The reaction products after electrolysis were isolated in stages: the reaction mixture was degassed in an argon flow for 30 min, and the supporting electrolyte was precipitated with hexane being an extracting agent for sulfur-containing organic compounds.

The GC/MS spectra were recorded on a GCMS-QP2010 Ultra instrument (gas chromatograph coupled with mass spectrometer) (Shimadzu). Helium served as a carrier gas, and an SPB-1 SULFUR (30 m × 0.32 mm) capillary column packed with silica gel as an adsorbent at $T_{max} = 320°C$ was used. The chromatographic analysis of a mixture of the synthesized sulfur-containing organic compounds was carried out on a Kristall-Lyuks 4000M gas chromatograph with a flame photometric detector. IR spectra were recorded on an FSM 1201 FT-IR spectrometer (400–5000 cm^{-1}). X-ray fluorescence analysis was performed using an ASE-1 energy dispersive analyzer.

RESULTS AND DISCUSSION

Analysis of redox characteristics of complexes $Cr(3,6\text{-}SQ)_3$ and $In(3,6\text{-}SQ)_3$ is necessary for determining the stability of their redox states and for estimating metal–ligand interaction. The redox properties of the In(III) complex with the redox-active tris-*o*-semiquinolate ligands and the redox pair 3,6-di-*tert*-butylpyrocatechol ($3,6\text{-}QH_2$)/3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-Q) in dichloromethane were studied by cyclic voltammetry (CV) at the glassy carbon and platinum electrodes (Table 1).



M = Cr; In

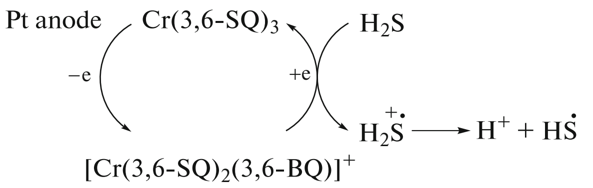
The indium(III) complex is reduced via three quasi-reversible steps and accompanied by a change in the oxidation state of the organic ligand. Two redox processes are detected in the anodic region, the first of which is quasi-reversible (Scheme 1).

$$\begin{tikzcd}
{[In(3,6\text{-}SQ)(3,6\text{-}Cat)_2]^{2-}} \arrow[r, shift left, "-e"] \arrow[d, shift left, "+e"] & {[In(3,6\text{-}SQ)_2(3,6\text{-}Cat)_2]^{-}} \arrow[l, shift left, "+e"] \arrow[r, shift left, "-e"] & In(3,6\text{-}SQ)_3 \arrow[l, shift left, "+e"] \arrow[r, shift left, "-e"] & {[In(3,6\text{-}SQ)_2(3,6\text{-}BQ)]^{+}} \arrow[l, shift left, "+e"] \arrow[d, "-e"] \\
{[In(3,6\text{-}Cat)_3]^{3-}} \arrow[u, shift left, "-e"] & & & {[In(3,6\text{-}SQ)(3,6\text{-}BQ)_2]^{2+}}
\end{tikzcd}$$

Scheme 1.

The further oxidation of the complex leads to the decoordination of free 3,6-Q. As compared to the earlier studied chromium(III) complex [11], the electrochemical reduction of the $In(3,6\text{-}SQ)_3$ complex occurs at high cathodic potentials, which is explained by the influence of the metal ion nature. At the same time, no significant differences in the redox potentials of the $3,6\text{-}QH_2/3,6\text{-}Q$ transition are observed in the anodic region.

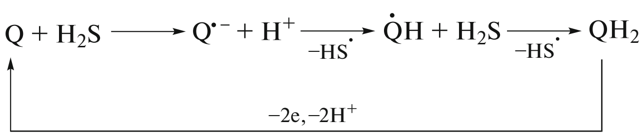
The first one-electron quasi-reversible step and the ability of the complexes to form a relatively stable monocationic species make it possible to consider them as mediators of electron transfer in the reaction with hydrogen sulfide (Scheme 2).



Scheme 2.

The CV method is a convenient tool for the preliminary evaluation of the efficiency of action of mediators, since CV allows one to measure the overvoltage of the process of hydrogen sulfide oxidation involving the Cr(3,6-SQ)$_3$ and In(3,6-SQ)$_3$ complexes compared to the direct anodic activation of H_2S. In the presence of H_2S, the complexes are characterized by a catalytic increase in the cathodic peak current that characterizes the ability of the oxidized forms to act as mediators of one-electron hydrogen sulfide oxidation. The thiyl radical can be generated in this reaction both in the presence of the single-cation species of the mediators and using the electrochemical activation of H_2S considered earlier [16–20].

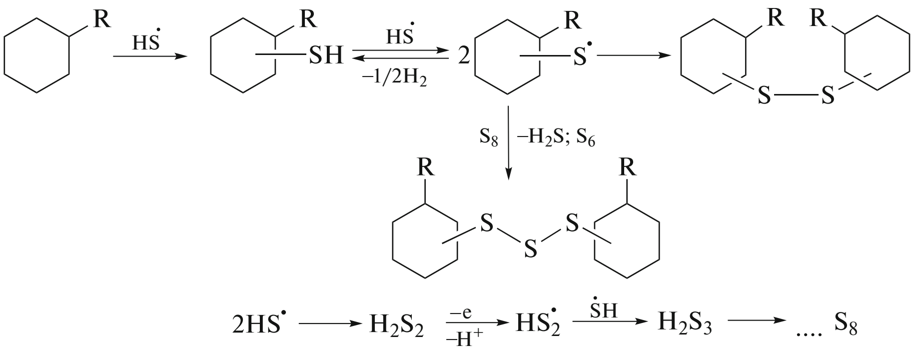
It is known that sterically hindered *o*-benzoquinones are efficient one-electron oxidants of hydrogen sulfide capable of reoxidizing QH_2 with air oxygen [21]. However, a negative point of their use is a restricted number of reaction–regeneration cycles, which does not allow one to achieve the quantitative yield of the products of the reactions of H_2S with organic compounds. Therefore, it seems reasonable to use the electromediatory systems including the free or coordinated *o*-semiquinone/*o*-benzoquinone redox pair and the platinum electrode necessary for the cyclic electrochemical regeneration of 3,6-QH_2 or the metal complex (Scheme 3).



Scheme 3.

In this work, we compared the mediators based on the chromium(III) and indium(III) complexes using the 3,6-QH_2/3,6-Q redox pair in the oxidation of H_2S in the presence of cycloalkanes. The problem of stability of the metal complexes is directly related to the ligand environment, since their organic fragments are prone to degradation to the highest extent. The efficiency of using the chromium(III) and indium(III) complexes with the redox-active ligands in the reactions involving H_2S is caused by the enhancement of their Lewis acidity due to the coordination of the redox-active ligand by the metal center.

The reactions of H_2S with cycloalkanes (cyclohexane, methylcyclohexane, cycloheptane, and ethylcyclohexane) were carried out in CH_2Cl_2 at 25°C under the conditions of electrolysis, the potential of which was varied depending on the type of the redox system (Cr(3,6-SQ)$_3$, In(3,6-SQ)$_3$, 3,6-QH_2/3,6-Q). The key intermediate of the considered reactions in the presence of the mediators is the thiyl radical reacting with cycloalkanes (Scheme 4).



Scheme 4.

As a result, cycloalkanethiols were obtained (1.68–1.74 V), whose further electrochemical transformations in the presence of the mediators led to organic disulfides (1.54–1.66 V) and trisulfides (1.76–1.82 V) (Table 2). The composition of a mixture of the reaction products is independent of the type of the electromediatory system and degree of substrate substitution. It follows from the data in Table 2 that cycloheptane is characterized by a higher reactivity in the reaction with the thiyl radical in the series of the studied cycloalkanes. The most efficient mediator is Cr(3,6-SQ)$_3$, which is explained by its stability toward hydrogen sulfide [11]. In the course of electrolysis, the indium(III) complex undergoes transformations accompanied by the decoordination and formation of sterically hindered *o*-benzoquinone. As a result, the yield of the reaction products using this mediator insignificantly differs from the parameters obtained for the 3,6-QH_2/3,6-Q redox pair.

Table 2. Current efficiency of the sulfur-containing compounds/cycloalkanethiols (%) synthesized by the reactions of hydrogen sulfide with cycloalkanes in the presence of various redox systems (τ = 90 min)

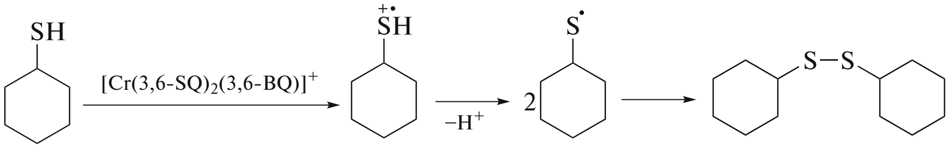
Compound	$Cr(3,6\text{-}SQ)_3$	$In(3,6\text{-}SQ)_3$	$3,6\text{-}QH_2/3,6\text{-}Q$
C_6H_{12}	40.6/10.2	25.7/5.7	26.9/2.6
$C_6H_{11}(CH_3)$	48.5/7.6	22.1/4.6	26.3/2.6
C_7H_{14}	52.1/8.4	27.7/5.3	29.9/4.6
$C_6H_{11}(C_2H_5)$	45.8/17.8	19.9/4.0	16.8/3.4

The dependences of the yield and composition of the reaction products on the time of electrosynthesis were studied for the reaction of hydrogen sulfide with cycloheptane under the conditions of the electrochemical oxidation of the $Cr(3,6\text{-}SQ)_3$ complex (Fig. 1).

It was found that after 30 min of electrolysis the yield of cycloheptanethiol decreased because of its transformation into the corresponding disulfide with a simultaneous increase in the yield of trisulfides, which is related to the formation of inorganic sulfanes from hydrogen sulfide in a solution (Scheme 4).

In the case of using the $In(3,6\text{-}SQ)_3$ complex, whose monocationic form is instable in time, di- and trisulfides are predominantly formed in approximately equal amounts as the target products of the reactions of cycloheptane and methylcyclohexane with H_2S: for C_7H_{14}, 11.4 and 12.9%; for $C_6H_{11}(CH_3)$, 11.6 and 10.5%. In the presence of the $3,6\text{-}QH_2/3,6\text{-}Q$ redox pair, the content of disulfides obtained from hydrogen sulfide and methylcyclohexane is by two times higher than their concentration obtained as a result of the reaction of H_2S and cycloheptane. The yields of disulfides were 14.8 and 7.9%.

The accumulation rates of the reaction products were examined for the reaction of hydrogen sulfide with cyclohexane in the presence of the electrochemically activated form of the $In(3,6\text{-}SQ)_3$ complex (Fig. 2). As follows from the data in Fig. 2, the mixture of sulfur-con taining products contains all the three components (RSH, RSSR, and RS_3R) within a short reaction time (30 min). This indicates the consecutive—parallel steps of the studied transformations. A sufficiently high yield of disulfides for 30 min is explained by two routes of the formation of cyclohexylthiyl radicals: (1) the reaction of the HS radical with cyclohexanethiol (Scheme 4) and (2) the oxidation of thiol by the mediator (Scheme 5).



Scheme 5.

The yield of disulfide remains almost unchanged in time, which is due to a higher rate of the reaction of cyclohexylthiyl radicals with sulfur and the accumulation of stable trisulfides.

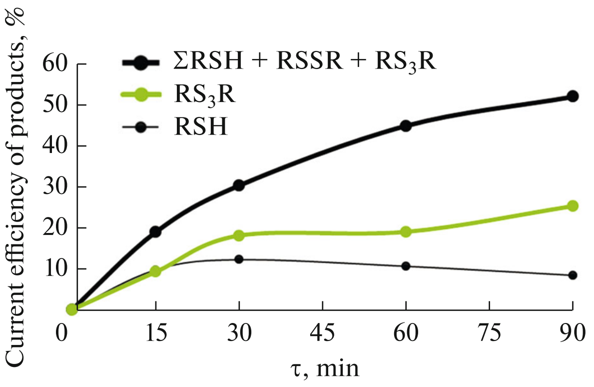


Fig. 1. Current efficiency of the sulfur-containing compounds synthesized by the reaction of hydrogen sulfide with cycloheptane using the chromium(III) complex vs. time.

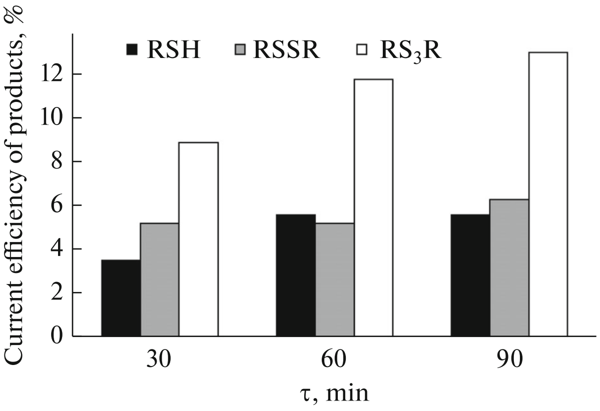


Fig. 2. Current efficiency of the sulfur-containing compounds synthesized by the reaction of hydrogen sulfide with cyclohexane using the indium(III) complex vs. time.

The selectivity in three routes of the reaction (RSH, RSSR, and RS_3R) is almost independent of the substrate nature. It was shown for the reaction of hydrogen sulfide with ethylcyclohexane that the selectivity to thiol varied depending on the type of the mediator: 38.8 ($Cr(3,6\text{-}SQ)_3$), 20.0 ($In(3,6\text{-}SQ)_3$), and 15.4% ($3,6\text{-}QH_2/3,6\text{-}Q$). Organic trisulfides are predominantly formed in the reactions of H_2S with cycloheptane and methylcyclohexane when using $Cr(3,6\text{-}SQ)_3$ and, therefore, the selectivity in this route is 85.1 and 89.6%, respectively, within 60 min.

In the case of the $Cr(3,6\text{-}SQ)_3$ complex, the content of formed sulfur (Scheme 4) is by ~1.5 times lower than that when using the indium(III) complex and *o*-quinone as mediators, due to the participation of S_8 in the formation of trisulfides. The degree of regeneration of the $Cr(3,6\text{-}SQ)_3$ complex reaches a maximum (95.0%), unlike the $3,6\text{-}QH_2/3,6\text{-}Q$ redox pair (80.2%), which explains a higher yield of sulfur and sulfur-containing compounds.

To conclude, we developed for the first time the promising method for the indirect oxidation of H_2S in the presence of the mediators based on the chromium(III) and indium(III) complexes with the 3,6-di-*tert*-butyl-*o*-semiquinolate ligand and the redox pair 3,6-di-*tert*-butylpyrocatechol/3,6-di-*tert*-butyl-*o*-benzoquinone in the reactions with unsubstituted and alkyl-substituted cycloalkanes. The application of the mediators considered in the work decreases energy consumptions compared to the anodic activation of H_2S by 0.4–0.7 V. The use of metal complexes as mediators of electron transfer in the reactions of H_2S with cycloalkanes is efficient, available, and ecologically friendly, especially in comparison with the traditional methods of organic synthesis.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 17-13-01168.

REFERENCES

1. Francke, R. and Little, R.D., *Chem. Soc. Rev.*, 2014, vol. 43, p. 2492.
2. Magdesieva, T.V. and Butin, K.P., *Usp. Khim.*, 2002, vol. 71, no. 3, p. 255.
3. Ogibin, Yu.N., Elinson M.N., and Nikishin, G.I., *Usp. Khim.*, 2009, vol. 78, no. 2, p. 99.
4. Butin, K.P., Beloglazkina, E.K., and Zyk, N.V., *Usp. Khim.*, 2005, vol. 74, no. 6, p. 585.
5. Magdesieva, T.V. *Elektrokhimiya organicheskikh soedinenii v nachale XXI veka* (Electrochemistry of Organic Compounds in the Beginning of the 21st Century), Gul'tyaya, V.P., Krivenko, A.G., and Tomilov, A.P., Eds., Moscow: Sputnik+, 2008, p. 147.
6. Budnikova, Yu.G., *Usp. Khim.*, 2002, vol. 71, no. 2, p. 126.
7. Berberova, N.T., Shinkar', E.V., Smolyaninov, I.V., and Okhlobystin, A.O., *Vovlechenie serovodoroda, tiolov i polisul'fanov v sintez organicheskikh soedinenii sery* (Involvement of Hydrogen Sulfide, Thiols, and Polysulfanes into the Synthesis of Organic Sulfur Compounds), Rostov-on-Don: YuNTs RAN, 2009.
8. Okhlobystin, A.O., Okhlobystina, A.V., Shinkar', E.V., et al., *Dokl. Ross. Acad. Nauk*, 2010, vol. 435, no. 3, p. 1.
9. Steckhan, E., *Top. Curr. Chem.*, 1987, vol. 142, p. 1.
10. Steckhan, E., *Angew. Chem., Int. Ed. Engl.*, 1986, vol. 25, p. 683.
11. Okhlobystin, A.O., Smolyaninov, I.V., Okhlobystina, A.V., et al., *Russ. J. Coord. Chem.*, 2013, vol. 39, no. 1, p. 33.
12. Kapre, R.R., Bothe, E., Weyhermuller, T., et al., *Inorg. Chem.*, 2007, vol. 46, no. 19, p. 7827.
13. Piskunov, A.V., Maleeva, A.V., Fukin, G.K., et al., *Dalton. Trans.*, 2011, vol. 40, p. 718.
14. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
15. *Handbook on Preparative Inorganic Chemistry*, Brauer, G., Eds., New York: Academic, 1965, vol. 4.
16. Smolyaninov, I.V., Okhlobystin, A.O., Poddel'skii, A.I., et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 1, p. 14.
17. Berberova, N.T., Shinkar', E.V., Smolyaninov, I.V., and Okhlobystina, A.V., *Serovodorod i alkantioly v sinteze biologicheski aktivnykh organicheskikh proizvodnykh sery* (Hydrogen Sulfide and Alkanethiols in the Synthesis of Biologically Active Sulfur Compounds), Rostov-on-Don: YuNTs RAS, 2016.
18. Berberova, N.T., Shinkar', E.V., Smolyaninov, I.V., and Pashchenko, K.P., *Dokl. Ross. Akad. Nauk*, 2015, vol. 465, no. 6, p. 683.
19. Shinkar', E.V., Shevtsova, A.V., Sediki, D.B., and Berberova, N.T., *Russ. J. Electrochem.*, 2015, vol. 51, no. 11, p. 1046.
20. Berberova, N.T., Shinkar', E.V., Smolyaninov, I.V., and Abdulaeva, V.F., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 4, p. 998.
21. Berberova, N.T. and Shinkar', E.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 7, p. 1182.

Translated by E. Yablonskaya