

## An Organosilicon Sorbent with Dithiocarbamate Groups

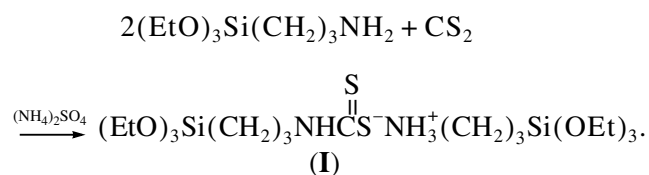
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Organic derivatives of dithiocarbamates are finding extensive practical use. Many of them possess specific biological activities and are recommended as medicinal drugs [1, 2]. An important field of practical application of organic compounds containing dithiocarbamate groups is their use as reagents to determine heavy metal ions [3–5] and to purify wastewaters from toxic contaminants [6, 7]. Sorbents with dithiocarbamate groups have been reported [8, 9].

While developing the research into carbofunctionally substituted organosilicon monomers and materials for sorption based on them [10, 11], we synthesized and studied an organosilicon sorbent containing dithiocarbamate groups.

The initial monomer, 3-triethoxysilylpropylammonium 3-triethoxysilylpropylthiocarbamate (**I**), was prepared in 76% yield by the condensation of 3-triethoxysilylpropylamine with carbon disulfide in the presence of catalytic amounts of ammonium sulfate (60°C, 7 h).



Compound **I** is a pale yellow liquid, mp 185–187°C (0.02–0.03 mmHg),  $n_D^{20}$  1.5000.

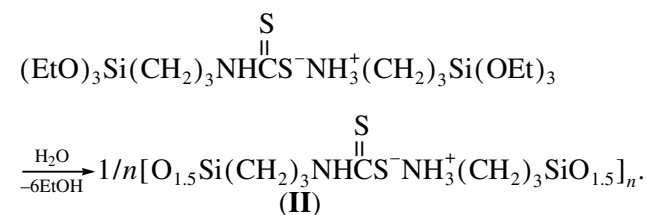
For  $\text{Si}_2\text{C}_{19}\text{H}_{46}\text{N}_2\text{S}_2\text{O}_6$  anal. calcd. (%): C, 43.98; H, 8.93; N, 5.40; S, 12.36; Si, 10.82.

Found (%): C, 43.67; H, 8.70; N, 6.13; S, 12.65; Si, 11.32.

IR (v,  $\text{cm}^{-1}$ ): 3220, 2970, 1530, 1020 (NH), 1390 (C=S), 1090, 770 (SiOC), 960 (C–S).

The hydrolytic polycondensation of compound **I** in a weakly alkaline medium (pH 8–9) results in 3-poly(3-

silsesquioxanylpropylthiocarbamate)3-silsesquioxanylpropylammonium (**II**) in 96% yield.



The cross-linked polymer **II** was isolated as a pale yellow fine powder.

For  $\text{Si}_2\text{C}_7\text{H}_{16}\text{N}_2\text{S}_2\text{O}_3$  anal. calcd. (%): C, 28.36; H, 5.44; N, 9.44; Si, 18.94.

Found (%): C, 28.50; H, 5.27; N, 8.36; Si, 18.72.

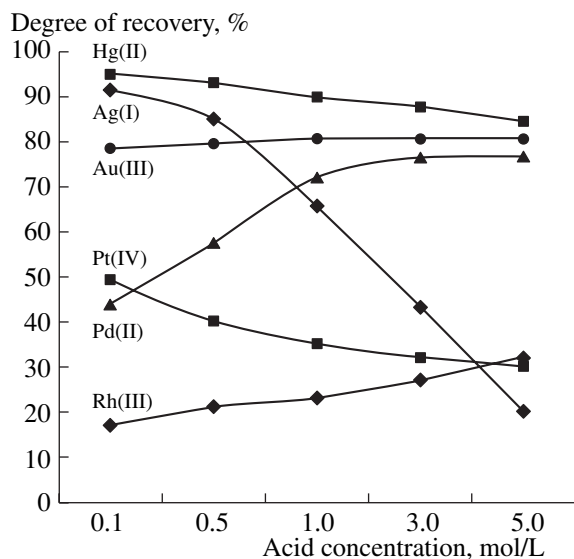
IR (v,  $\text{cm}^{-1}$ ): 3400, 2930, 1540, 1020 (NH), 2570 (S–H), 1340 (C=S), 1100 (Si–O–Si).

Polymer **II** is thermally stable up to 220°C; its specific weight ( $\text{g cm}^{-3}$ ) is 0.58 (bulk), 1.24 (true), and 0.55 (apparent); the porosity is 56%; and the total pore volume is  $1.01 \text{ cm}^3 \text{ g}^{-1}$ . Polymer **II** acquires a yellow color on saturation with Hg(II), orange with Au(III), beige with Pt(IV), brown with Pd(II), pink with Rh(III), and primrose with Ag(I).

The sorption activity of polymer **II** was studied with respect to Hg(II), Au(III), Pt(IV), Pd(II), and Rh(III) in solutions (0.1–5.0 mol/L) of hydrochloric acid and with respect to Ag(I) in solutions of nitric acid.

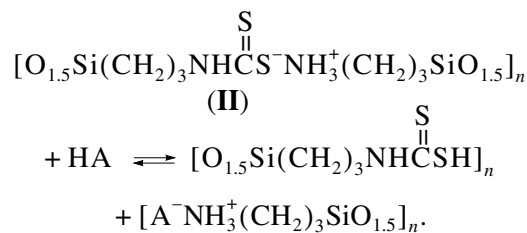
The acid concentration has the most pronounced effect on the degree of recovery of Ag(I) and Pd(II) (Fig. 1). However, these effects are opposite. When Ag(I) is extracted from solutions of nitric acid, an increase in the proton concentration results in suppression of sorption due to the competing reaction of the  $\text{H}^+$  ions with the thiolate sulfur atom. The extraction of Pd(II) ( $[\text{PdCl}_4]^-$ ) and Rh(III) ( $[\text{RhCl}_6]^{3-}$ ) chloride complexes is facilitated by an increase in the concentration of chloride ions in the solution, which corresponds to an increase in the stability of chloride complexes of these elements. The least pronounced influence of the hydrochloric acid concentration is noted for the sorption of Hg(II) and Au(III).

In solutions of acids, polymer (**II**) is transformed through the reaction of the dithiocarbamate fragment



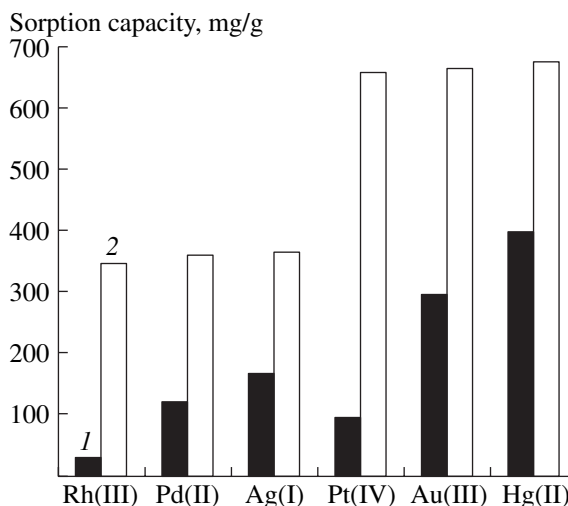
**Fig. 1.** Effect of the acid concentration on the degree of recovery of Hg(II), Ag(I), Au(III), Pt(IV), Pd(II), and Rh(III).

with the acid molecule (HA), which apparently goes to equilibrium:

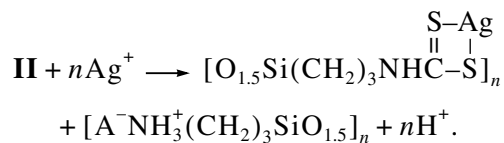


The existence of this equilibrium in the sorbent-solution system is indicated by the absorption band at  $1500\text{ cm}^{-1}$  due to asymmetric vibrations of the  $\text{NH}_3^+$  group, which appears in the IR spectrum of polymer **II** treated with a nitric acid solution. Sorption in nitric acid solutions also gives rise to an intense band at  $1380\text{ cm}^{-1}$  ( $\nu_{\text{NO}_3^-}$ ) in the IR spectrum of complex **II**, which is missing in the spectrum of the free sorbent, indicating that nitrate anions are inserted into the polymer structure. Protonation of the functional group in polymer **II** entails an increase in the pH upon contact with weakly alkaline solutions.

This behavior of polymer **II** in acid solutions determines the ion coordination properties of its functional groups and the observed pattern of influence of the acid concentration on the degree of recovery of metal ions (Fig. 1). The Hg(II) and Ag(I) ions most probably react with both sulfur atoms according to the ion coordination mechanism:



**Fig. 2.** (1) SSC and (2) FSC values for polymer **II**.



This can be proved, in particular, by the fact that the IR spectrum of polymer **II** saturated with Hg(II) or Ag(I) no longer exhibits bands at  $1340\text{ cm}^{-1}$  (C=S) or  $2570\text{ cm}^{-1}$  (S-H). The bands corresponding to vibrations of the amine ( $1540\text{ cm}^{-1}$ ) and ammonium ( $1500\text{ cm}^{-1}$ ) groups do not undergo any visible changes. The significant proportion of the ion exchange constituent in the sorption of  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  cations is confirmed by the quantitative desorption of these cations by 6 M nitric acid solutions.

The reactions of the anionic complexes  $\text{AuCl}_4^-$ ,  $\text{PtCl}_6^-$ ,  $\text{PdCl}_4^{2-}$ , and  $\text{RhCl}_6^{3-}$  with the functional groups of polymer **II** involve apparently both the nitrogen and sulfur atoms. This is indicated by the absence of the band at  $1500\text{ cm}^{-1}$  ( $\text{NH}_3^+$ ) in the IR spectra of polymer **II** saturated with these ions and by the forms in which these ions are incorporated in the polymeric matrix. According to elemental analysis, sorbent **II** saturated with metal ions in solutions of HCl (3 mol/L) contains gold and palladium as  $\text{AuCl}$  and  $\text{PdCl}_{0.5}$ . This means that the metal atoms are coordinated to at least three atoms of functional groups (the coordination number is 4). The IR spectra of polymer **II** saturated with Au(III), Pt(IV), Pd(II), or Rh(III) no longer contains the band at  $1340\text{ cm}^{-1}$  (C=S), while the bands at  $3400$  and  $1540\text{ cm}^{-1}$  (NH) are shifted to longer wavelengths. These data, together with the low (not more than 5–10%) desorption of gold, platinum, palladium, and rhodium on treatment with 6–9 M nitric or hydrochloric acid, imply the predominant ion coordination

interaction of the anionic complexes of these elements with ammonium and amine nitrogen atoms and the thione sulfur atom. The degree of involvement of the ammonium group probably decreases with an increase in the HCl concentration due to its anion exchange interaction with chloride anions. In solutions of hydrochloric acid with a concentration of 5 mol/L, gold and platinum enter the sorbent phase as AuCl<sub>2</sub> and PdCl<sub>2</sub>.

The static sorption capacity (SSC) values were determined in 3 M solutions of acids. Comparison of the experimental SSC values with theoretical values of full sorption capacity (FSC) (Fig. 2) calculated from the content of functional groups with the assumption that 1 : 1 complexes are formed in the sorbent phase demonstrated that the degree of occupation of chemically active groups (SSC · 100/FSC) of polymer **II** decreases in the sequence Hg(II) (59%), Ag(I) (46%), Au(III) (45%), Pd(II) (33%), Pt(IV) (14%), and Rh(III) (9%). This sequence is in line with known data on the complexing activity of sulfur-containing organic sorbents and reagents [12] and also correlates with the solubility products of the sulfides of these metals.

The times it takes for sorption equilibrium to be established in 3 M acid solutions for the metal ions in question are as follows: 2 h for Hg(II), 3 h for Ag(I), 2 h for Au(III), 1.5 h for Pd(II), 3 h for Pt(IV), and 3 h for Rh(III).

Thus, poly(3-silsesquioxanylpropylthiocarbamate)3-silsesquioxanylpropylammonium, which we prepared, is an efficient sorbent for the recovery of mercury and noble metal ions from acid solutions. In terms of the SSC values, especially those with respect to Hg(II) and Au(III), this sorbent is not inferior to the most efficient known organosilicon and organic sulfur- and nitrogen-containing sorbents [10–12].

## ACKNOWLEDGMENTS

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## REFERENCES

1. Yilmaz, V.T., Yazicilar, T.K., Cesur, H., *et al.*, *Synth. React. Inorg. Metal-Org. Chem.*, 2003, vol. 33, no. 4, pp. 589–605.
2. US Patent no. 6407135, *Ref. Zh. Khim.*, 2003, no. 190.86P.
3. Dominguez, O., Asuncion, A.M., and Arcos, M.J., *Electroanalysis*, 2002, vol. 14, nos. 15/16, pp. 1083–1089.
4. Mekhmet, Ya., *Zh. Anal. Khim.*, 2003, vol. 58, no. 5, pp. 513–516.
5. Igarashi, S., Takahashi, A., Ueki, Y., and Yamaguchi, H., *Analyst*, 2000, vol. 125, no. 5, pp. 797–798.
6. Erven, C.A., *Metal. Finish.*, 2001, vol. 99, no. 1, pp. 8–19.
7. Ignatkina, V.A., *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 2001, no. 1, pp. 4–7.
8. Denizli, A., Kesenci, K., Arica, Y., and Piskin, E., *React. Funct. Polym.*, 2000, vol. 44, no. 3, pp. 235–243.
9. Venkatesan, K.A., Srinivasan, T.G., and Vasudeva, R.P.R., *Separ. Sci. Technol.*, 2002, vol. 37, no. 6, pp. 1417–1429.
10. Voronkov, M.G., Vlasova, N.N., and Pozhidaev, Yu.N., *Zh. Prikl. Khim. (S.-Peterburg)*, 1996, vol. 69, pp. 705–718.
11. Voronkov, M.G., Vlasova, N.N., and Pozhidaev, Yu.N., *Appl. Organomet. Chem.*, 2000, vol. 14, pp. 287–303.
12. Murinov, Yu.I., Maistrenko, V.N., and Afzaletdinova, N.G., *Ekstraksiya metallov S,N-organicheskimi soedineniyami* (Extraction of Metals by S,N-Containing Organic Compounds), Moscow: Nauka, 1993.