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# LIPOPHILIC POLYTHIAMACROCYCLES AS PALLADIUM EXTRACTING AGENTS

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## Abstract

Six new lipophilic thiacrown ethers (1-6), abbreviated as 2-octyl-9S3, 2-octyl-10S3, 2-octyl-12S4, 6-octyl-14S4, 3-octyl-16S4 and dioctyl-18S6, were synthesized starting from different dithiols and dihalides. $Cs_2CO_3$ is used for the cyclizations. The extraction behavior of palladium (II) from nitric acid media with these reagents in chloroform has been studied in terms of extraction equilibrium constants $K_{ex}$. The influence of parameters such as lipophilicity brought by alkyl chains, macrocyclic cavity size and number of sulfur donor atoms on the extraction behavior was investigated.

## Introduction

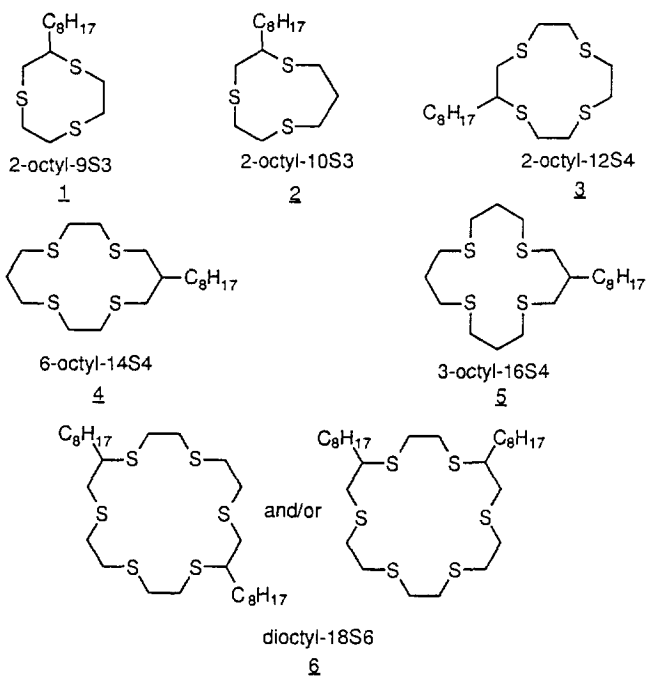
The continuing high prices of the precious metals have ensured that there is much interest in developing new ways of extracting, concentrating and separating them. Nitrate waste solutions of PUREX (Plutonium Uranium Recovery by Extraction) process contain appreciable amounts of palladium which can be recovered for commercial utilization[1,2].

It is well known that towards soft metal cations ($Cu^+$, $Pd^{2+}$, $Ag^+$, $Pt^{2+}$ and $Hg^{2+}$) thiacrown ethers are excellent complexing agents[3,4,5]. In order to transfer quantitatively the $Pd^{2+}$/thiacrown ether complexes in organic solution by solvent extraction it is necessary to employ lipophilic thiacrown ethers. Here we describe the synthesis of new lipophilic thiacrown ethers of various cavity sizes and topology.

## Results and Discussion

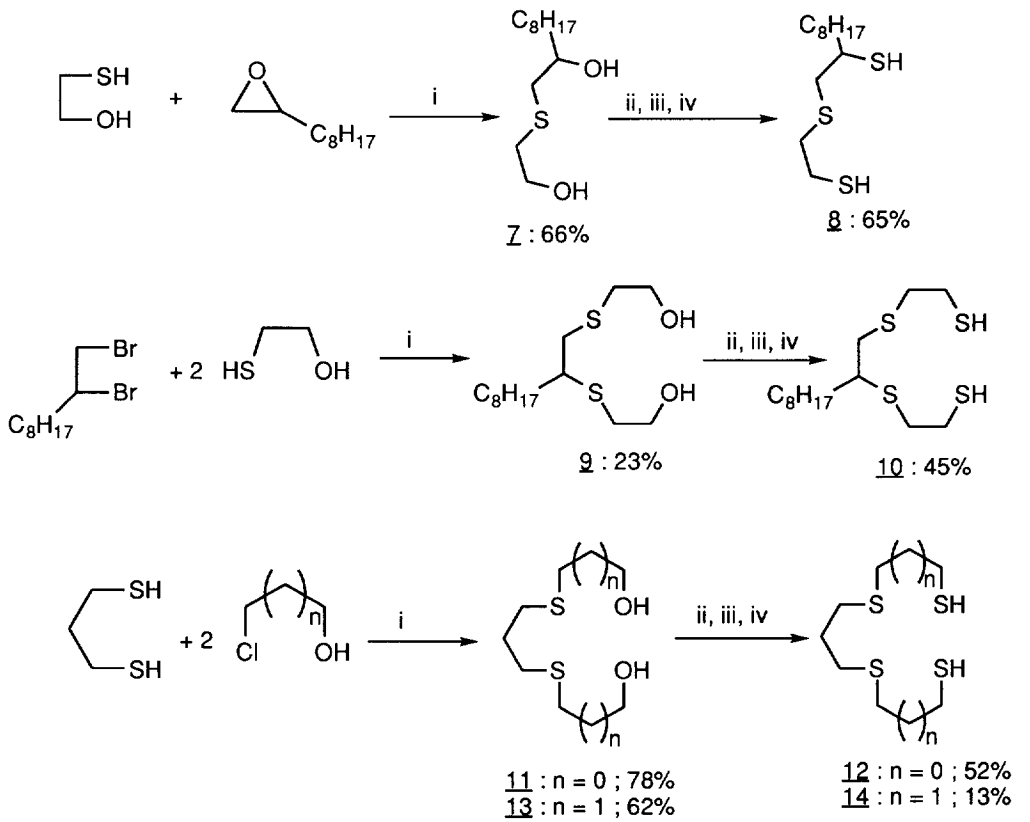
**Synthesis.** The lipophilic thiacrown ethers studied (1-6, chart I) were prepared in a manner similar to that reported by Buter and Kellogg[6] : a dihalide was allowed to react with a cesium dithiolate under high-dilution conditions in DMF as solvent. This synthetic route avoid using β-halo-sulfides which are potent vesicants. In this fashion, 2-octyl-1,4,7-trithiacyclononane 1, 2-octyl-1,4,7-trithiacyclodecane 2, 2-octyl-1,4,7,10-tetrathiacyclododecane 3, 6-octyl-1,4,8,11-tetrathiacyclotetradecane 4 and 3-octyl-1,5,9,13-tetrathiacyclohexadecane 5 were obtained. 2,11 (and/or 2,15)-dioctyl-1,4,7,10,13,16-hexathiacyclooctadecane 6 was isolated from the preparation of 1. Since systematic names of these thiacrown ethers are too cumbersome for repeated use, the trivial naming system proposed in chart I, which is inspired by the abbreviated nomenclature introduced by Ochrymowycz[7], will be used hereafter.

**Chart I. Code Numbers and Trivial Names of Lipophilic Thiacrown Ethers Prepared in this Study.**



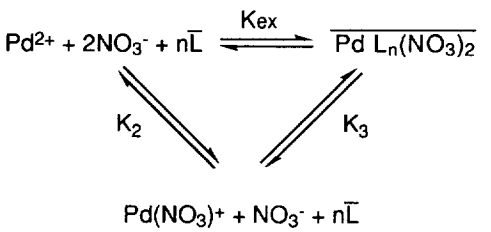

Dithiols 8, 10, 12 and 14 of scheme I are the thiacrown ethers precursors. They were prepared by treatment of the corresponding dialcohols, 7, 9, 11 and 13 respectively, with excess thiourea in concentrated hydrochloric acid followed by hydrolysis with base. To our knowledge, compounds 1-10, 13 and 14 have not been reported previously.

**Scheme I. Syntheses of the Dithiols.**




i, NaOEt/EtOH ; ii, thiourea, conc HCl ; iii, KOH (or NaOH)/$H_2O$ ; iv, HCl/$H_2O$.

**Extraction Studies.** Palladium is considered to be extracted by a ligand L in a ratio of 1 to n from nitric acid media according to the following reaction scheme, where the overline denotes the species existing in the organic phase :




The extraction constant Kex, calculated from $Pd^{2+}$, and the stability constant $K_2$ are given by Eqs. 1 and 2 respectively :

$$K_{ex} = \frac{\overline{[PdL_n(NO_3)_2]}}{[Pd^{2+}]\,[NO_3^-]^2\,[\bar{L}]^n} \quad (1)$$

$$K_2 = \frac{[Pd(NO_3)^+]}{[Pd^{2+}]\,[NO_3^-]} \quad (2)$$

The total concentration of unextracted Pd (II) is expressed as follows :

$$[Pd(II)_t] = [Pd^{2+}] + [Pd(NO_3)^+] \quad (3)$$

From Eqs. 2 and 3, we obtain :

$$[Pd^{2+}] = \frac{[Pd(II)_t]}{1 + K_2[NO_3^-]} \quad (4)$$

Substitution of Eq. 4 into Eq. 1 gives the following equation, in which all terms are known :

$$K_{ex} = \frac{\overline{[PdL_n(NO_3)_2]}\,(1 + K_2[NO_3^-])}{[Pd(II)_t]\,[NO_3^-]^2\,[\bar{L}]^n} \quad (5)$$

The unextracted palladium concentration $\underline{[Pd(II)_t]}$ is determined by atomic absorption. The extracted palladium concentration $\overline{[PdL_n(NO_3)_2]}$ can be calculated with Eq. 6 where subscript i refers to initial conditions :

$$\overline{[PdL_n(NO_3)_2]} = [Pd(II)_t]_i - [Pd(II)_t] \quad (6)$$

The $K_2$ value is estimated[8] at 1.2 L.mol$^{-1}$. If the nitric acid concentration $[HNO_3]$ is fixed at 2 mol.L$^{-1}$ in order to be comparable to the acidity of fission products solutions of PUREX process, then $[NO_3^-]$ is in large excess with regard to other species, so nearly equal to its initial concentration and considered constant. The stoichiometric parameter n is deduced from those observed for unsubstituted thiacrown ethers[9] and the free extractant concentration $[\bar{L}]$ is given by Eq. 7 :

$$[\bar{L}] = [\bar{L}]_i - n\overline{[PdL_n(NO_3)_2]} \quad (7)$$

Extraction of aqueous palladium nitrate was carried out at 25°C with chloroform solutions of thiacrown ethers 1-6. For comparison purposes, di-n-hexyl sulphide (DHS), which is used on an industrial scale for the production of palladium in non-nuclear area[10], was also tested. Table I gives the $K_{ex}$ values.

**Table I. Equilibrium Constants $K_{ex}$ for Extraction of Palladium Nitrate with DHS and Thiacrown Ethers[a].**

| Entry | Extractant | n | $K_{ex}$ |
|---|---|---|---|
| 1 | DHS | 2[b] | 21 700 000 $mol^{-4}.L^4$ |
| 2 | 2-octyl-9S3 | 2 | 82 000 000 $mol^{-4}.L^4$ [c] |
| 3 | 2-octyl-10S3 | 2 | 54 000 000 $mol^{-4}.L^4$ |
| 4 | 2-octyl-12S4 | 1 | 0 |
| 5 | 6-octyl-14S4 | 1 | 135 $mol^{-3}.L^3$ |
| 6 | 3-octyl-16S4 | 1 | 14 000 $mol^{-3}.L^3$ |
| 7 | dioctyl-18S6 | 1 | 1 226 000 $mol^{-3}.L^3$ [d] |

[a] 2M $HNO_3$-chloroform system at 25°C ; $[Pd(II)]_i = 10^{-3}M$ ; [b] Data from ref 10 ; [c] 87 % of Pd extracted ; [d] 98 % of Pd extracted.

As can be seen from entries 1-3, where 1:2 palladium-extractant complexes are formed, 2-octyl-9S3 1 shows the highest extraction constant. This may be attributable to the fact that all sulfur atoms are endodentate (the lone pairs are directed towards the center of the ring) in a 9S3 skeleton[11]. Since a conformational change is unnecessary during the complexation, metal ion binding strength is increased. 2-octyl-10S3 2 has a lower extraction constant : one might assume that its sulfur donor atoms adopt less established endodentate positions. Compounds 1 and 2 are, anyway, highly more efficient than DHS, whose extraction rate of palladium is moreover very slow (for lipophilic thiacrown ethers, the equilibrium is reached within a few minutes compared with the 10 hours required for DHS).

As can be seen from entries 4-7, where 1:1 palladium-extractant complexes are formed, dioctyl-18S6 6 shows the highest extraction constant. This might be explained by several hypothesis. First, the strong lipophilic character of this thiacrown ether, due to its two octyl chains, may result into an increased extraction of the ion-pair compound. Secondly, the two remaining non-bonded sulfur atoms of a 18S6 skeleton contribute to stabilization of the complex by giving weak interactions with the central $Pd^{2+}$ ion[12]. Thirdly, since the 18S6 skeleton has both endo- and exodentate sulfur atoms[13], conformation changes to the endodentate conformation should be less important than those occurred for the other tetradentate thiacrown ether skeletons who have only

exodentate sulfur atoms. In addition to this and as Desper and Gellman mentioned it[14], peripheral modifications with several alkyl chains can force the sulfur atoms to adopt endodentate positions. Therefore, dioctyl-18S6 6 is "well-preorganized" for complexation. For thiacrown ethers 4 and 5, ion-pair compounds formed in aqueous phase are moderately lipophilic which results in lower extraction constants. Most surprising is the anomalous behavior of 2-octyl-12S4 3 who does not extract palladium at all. This might be explained by the octyl chain which is not lipophilic enough to make the 12S4 skeleton efficient for extraction. Lipophilic character of simple 12S4 is extremely low : its solubility in chloroform reaches only 0.051 mol.L$^{-1}$.

In conclusion, most of the lipophilic thiacrown ethers we have synthesized exhibit high extraction properties towards palladium contained in nitric acid solutions. This may lead to the development of a new industrial technique for the removal of palladium from concentrated fission products solutions of nuclear fuel reprocessing.

## Experimental Section.

**General Methods**. Melting points were measured with a Buchi Melting Point Apparatus. Infrared spectra were obtained on a Philips PU 9716 spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Brüker AC 200 instrument in deuteriochloroform . A Perkin-Elmer M 1100 atomic absorption spectrophotometer was used for the determination of palladium. Elemental analysis was performed by Wolff Laboratories (Clichy, France).

Compounds cited without references were commercially available or prepared by unexceptional procedures. All reported yields are of isolated products.

**1-octyl-3-thia-pentane-1,5-diol** 7. In 50 mL of absolute ethanol under nitrogen, 1.15 g (0.05 mol) of sodium metal was dissolved. This mixture was warmed to 50°C and 3.9 g (0.05 mol) of 2-mercapto-ethanol was slowly added. To the resulting solution 7.8 g (0.05 mol) of 1,2-epoxy-decane was added and the mixture was then refluxed for 3 hr. The mixture was cooled at room temperature and the ethanol was removed by evaporation. The residue was taken up in 200 mL of $CH_2Cl_2$, washed with acidulated water, dried over $MgSO_4$ and the solvent was evaporated. Recrystallization from petroleum ether of the crude product gave 7.75 g (66%) of 7 as a white solid : mp 33-34°C ; $^1$H NMR ($CDCl_3$) δ 3.78 (t, 2H, J = 5.8 Hz, $OCH_2$) ; 3.70 (m, 1H, OCH) ; 2.79 (dd, 1H, J = 3.2 and 13.8 Hz, $SCH_2$) ; 2.77 (t, 2H, J = 5.8 Hz, $SCH_2$) ; 2.51 (dd, 3H, J = 8.6 Hz and 13.8 Hz, OH and $SCH_2$) ; 1.30-1.50 (m, 14H, $CH_2$) ; 0.82 (t, 3H, $CH_3$) ; IR (neat) 3600-3100, 2920, 2860, 1460, 1405, 1375, 1290, 1220, 1160, 1125, 1050, 1010 cm$^{-1}$.

**4-octyl-3,6-dithia-octane-1,8-diol** 9 was prepared by slowly adding 15 g (0.05 mol) of 1,2-dibromo-decane to a mixture of 2.3 g (0.10 mol) of sodium and 7.8 g (0.10 mol) of

2-mercapto-ethanol in 100 mL of absolute ethanol at 50°C under nitrogen. After refluxing for 3 hr, the mixture was cooled to room temperature and filtered. The ethanol was removed from the filtrate by evaporation. The residue was taken up in $CH_2Cl_2$, washed with water, dried over $MgSO_4$ and the solvent was evaporated. Chromatography of the crude product over $SiO_2$ with chloroform as eluent gave 6.7 g (23%) of 9 as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 3.70 (t, 4H, $OCH_2$) ; 3.40 (s, 2H, OH) ; 2.67-2.77 (m, 7H, $SCH_2$ and SCH) ; 1.42 (m, 2H, $CH_2$) ; 1.24 (m, 12H, $CH_2$) ; 0.84 (t, 3H, $CH_3$) ; IR (neat) 3600-3100, 2930, 2860, 1460, 1410, 1380, 1285, 1220, 1170, 1045 $cm^{-1}$.

**4,8-dithia-undecane-1,11-diol** 13 was prepared by slowly adding 47.27 g (0.50 mol) of 3-chloro-propanol to a mixture of 11.5 g (0.50 mol) of sodium and 27.06 g (0.25 mol) of propane-1,3-dithiol in 500 mL of absolute ethanol at 50°C under nitrogen. After refluxing for 3 hr, the workup procedure was carried out as described for 9. Distillation of the crude product gave 34.75 g (62%) of 13 as a colorless oil : bp 220°C (0.15 torr) ; $^1H$ NMR ($CDCl_3$) δ 3.74 (t, 4H, J = 6 Hz, $OCH_2$) ; 2.64 (t, 8H, $SCH_2$) ; 2.49 (s, 2H, OH) ; 1.78-1.95 (m, 6H, $CH_2$) ; IR (neat) 3600-3100, 2920, 2870, 1430, 1345, 1290, 1255, 1220, 1155, 1050 $cm^{-1}$.

**General Procedure for Preparation of Dithiols.** Each compound was prepared by refluxing 30 mmol of the corresponding diol, 5.02g (66 mmol) of thiourea and 16 mL of concentrated hydrochloric acid for 9 hr. The resulting solution was then cooled in an ice bath and 11.31 g (0.202 mol) of KOH (NaOH in case of 10) in 70 mL of water was cautiously added. This mixture was refluxed for 3 hr, allowed to cool, acidified with 10% hydrochloric acid and extracted twice with 100 mL of ether. The ethereal extract was dried over $MgSO_4$ and, after filtration, the ether was evaporated.

**1-octyl-3-thia-pentane-1,5-dithiol** 8 was prepared from 1-octyl-3-thia-pentane-1,5-diol 7 and was isolated by distillation (bp 150°C at 0.3 torr) in 65% yield as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 2.70-2.80 (m, 7H, $SCH_2$ and SCH) ; 1.75 (m, 2H, SH) ; 1.25-1.60 (m, 14H, $CH_2$) ; 0.88 (t, 3H, $CH_3$) ; IR (neat) 2930, 2860, 2550 $cm^{-1}$.

**4-octyl-3,6-dithia-octane-1,8-dithiol** 10 was prepared from 4-octyl-3,6-dithia-octane-1,8-diol 9 and was obtained, after chromatography over $SiO_2$ with heptane/ethyl acetate (95 : 5) as eluent, in 45% yield as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 2.64-2.84 (m, 11H, $SCH_2$ and SCH) ; 1.70-1.80 (m, 2H, SH) ; 1.41 (m, 2H, $CH_2$) ; 1.24 (m, 12H, $CH_2$) ; 0.85 (t, 3H, $CH_3$) ; IR (neat) 2930, 2860, 2545, 1595, 1530, 1460, 1430, 1380, 1270, 1215, 1140 $cm^{-1}$.

**4,8-dithia-undecane-1,11-dithiol** 14 was prepared from 4,8-dithia-undecane-1,11-diol 13 and was obtained, after chromatography over $SiO_2$ with heptane/ethyl acetate (95 : 5) as eluent, in 13% yield as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 2.57-2.66 (m, 12H, $SCH_2$) ; 1.80-1.95 (m, 6H, $CH_2$) ; 1.37 (t, 2H, SH) ; IR (neat) 2930, 2850, 2550, 1440, 1350, 1305, 1260, 1215 $cm^{-1}$.

**General Procedure for Preparation of Thiacrown Ethers.** $Cs_2CO_3$ (3.26 g, 10 mmol) was suspended in 550 mL of a well-stirred dry DMF solution at 60°C under $N_2$. A solution containing dithiol (10 mmol) and dihalide (10 mmol) in 100 mL of DMF was prepared. Half of this solution was added over 9 hr. Another 10 mmol of $Cs_2CO_3$ was added and the second half of the dithiol and dihalide solution was added over 9 hr. After complete addition, the reaction mixture was allowed to cool to room temperature. The DMF was removed under vacuum. The residue was taken up in $CH_2Cl_2$, washed with water, dried over $MgSO_4$ and the solvent was evaporated.

**2-octyl-9S3** 1 and **dioctyl-18S6** 6 were prepared from 1-octyl-3-thia-pentane-1,5-dithiol 8 and 1,2-dichloroethane. The crude product was chromatographed over $SiO_2$ with heptane/ethyl acetate (98 : 2) as eluent to afford 1 in 37% yield as a colorless oil and then by-product 6 in 24% yield as a colorless oil which slowly crystallized on standing : for 1 $^1H$ NMR ($CDCl_3$) δ 2.90-3.45 (m, 11H, $SCH_2$ and SCH) ; 1.27-1.60 (m, 14H, $CH_2$) ; 0.88 (t, 3H, $CH_3$) ; $^{13}C$ NMR ($CDCl_3$) δ (CH) 49.44 ; ($CH_2$) 39.77 , 36.56 , 35.44 , 35.30 , 34.24 , 33.42 , 31.72 , 29.33 , 29.31 , 29.11 , 27.07 , 22.52 ; ($CH_3$) 13.97 ; IR (neat) 2930, 2860, 1465, 1425, 1380, 1265, 1200 $cm^{-1}$ ; Anal. Calcd. for $C_{14}H_{28}S_3$ : C, 57.53 ; H, 9.59 ; S, 32.88. Found : C, 56.91 ; H, 9.59 ; S, 32.38 ; for 6 mp 68°C ; $^1H$ NMR ($CDCl_3$) δ 2.81 (m, 22H, $SCH_2$ and SCH) ; 1.27-1.60 (m, 28H, $CH_2$) ; 0.87 (t, 6H, $CH_3$) ; $^{13}C$ NMR ($CDCl_3$) δ (CH) 46.49 ; ($CH_2$) 38.69 , 33.94 , 33.04 , 32.75 , 32.58 , 32.52 , 31.74 , 31.51 , 29.34 , 29.14 , 26.69 , 22.54 ; ($CH_3$) 13.98 ; IR (neat) 2930, 2860, 1465, 1410, 1380, 1270 $cm^{-1}$ ; Anal. calcd. for $C_{28}H_{56}S_6$ : C, 57.53 ; H, 9.59 ; S, 32.88. Found : C, 57.88 ; H, 9.81 ; S, 31.90.

**2-octyl-10S3** 2 was prepared from 1-octyl-3-thia-pentane-1,5-dithiol 8 and 1,3-dibromopropane and was obtained, after chromatography over $SiO_2$ with heptane/ethyl acetate (98 : 2) as eluent, in 44% yield as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 2.60-3.40 (m, 11H, $SCH_2$ and SCH) ; 1.83 (quintet, 2H, $CH_2$) ; 1.25-1.65 (m, 14H, $CH_2$) ; 0.88 (t, 3H, $CH_3$) ; $^{13}C$ NMR ($CDCl_3$) δ (CH) 48.59 ; ($CH_2$) 39.13 , 36.45 , 34.16 , 32.28 , 31.73 , 30.29, 29.73 , 29.39 , 29.34 , 29.12 , 28.14 , 26.96 , 22.53 ; ($CH_3$) 13.99 ; IR (neat) 2930, 2860, 1460, 1430, 1410, 1380, 1345, 1275, 1260 $cm^{-1}$ ; Anal. Calcd. for $C_{15}H_{30}S_3$ : C, 58.82 ; H, 9.80 ; S, 31.37. Found : C, 58.71 ; H, 9.61 ; S, 31.59.

**2-octyl-12S4** 3 was prepared from 4-octyl-3,6-dithia-octane-1,8-dithiol 10 and 1,2-dibromoethane. The product 3 was purified by chromatography over $SiO_2$ with heptane/ethyl acetate (95 : 5) as eluent followed by recrystallization from $C_2H_5OH$ to afford 3 in 40% yield as a white solid : mp 72-74°C ; $^1H$ NMR ($CDCl_3$) δ 2.37-3.04 (m, 15H, $SCH_2$ and SCH) ; 1.31-1.61 (m, 14H, $CH_2$) ; 0.92 (t, 3H, $CH_3$); $^{13}C$ NMR ($CDCl_3$) δ (CH) 42.87 ; ($CH_2$) 35.48 , 32.37 , 31.75 , 29.53 , 29.40 , 29.29 (several carbon atoms) , 29.13 (several carbon atoms) , 28.92 , 28.81 , 26.77 , 22.54 ; ($CH_3$) 13.99 ; Anal. Calcd. for $C_{16}H_{32}S_4$ : C, 54.55 ; H, 9.09 ; S, 36.36. Found : C, 53.87 ; H, 8.79 ; S, 34.50.

**6-octyl-14S4** 4 was prepared from 3,7-dithia-nonane-1,9-dithiol 12[3] and 1-chloro-2-chloromethyl-decane and was obtained, after chromatography over $SiO_2$ with heptane/ethyl acetate (95 : 5) as eluent, in 19% yield as a white solid : mp 41°C ; $^1H$ NMR ($CDCl_3$) δ 2.50-2.80 (m, 16H, $SCH_2$) ; 1.95 (quintet, 2H, $CH_2$) ; 1.70-1.85 (m, 1H, CH) ; 1.27-1.50 (m, 14H, $CH_2$) ; 0.88 (t, 3H, $CH_3$) ; $^{13}C$ NMR (CDCl3) δ (CH) 38.60 ; ($CH_2$) 35.81 , 32.77 , 32.61 , 31.96 , 31.75 , 30.50 , 30.19 , 29.66 , 29.37 , 29.16 , 26.32 , 22.54 ; ($CH_3$) 13.99 ; Anal. Calcd. for $C_{18}H_{36}S_4$ : C, 56.84 ; H, 9.47 ; S, 33.68. Found : C, 57.07; H, 9.67 ; S, 33.61.

**3-octyl-16S4** 5 was prepared from 4,8-dithia-undecane-1,11-dithiol 14 and 1-chloro-2-chloromethyl-decane and was obtained, after chromatography over $SiO_2$ with hexane/ethyl acetate (95 : 5) as eluent, in 5% yield as a colorless oil : $^1H$ NMR ($CDCl_3$) δ 2.59-2.66 (m, 16H, $SCH_2$) ; 1.80-1.95 (m, 7H, $CH_2$ and CH) ; 1.26-1.50 (m, 14H, $CH_2$) ; 0.87 (t, 3H, $CH_3$).

**Palladium Extraction Experiments.** Commercially available DHS (Lancaster) was used without purification. Analytical-grade chloroform and distilled water were used. The aqueous phase was prepared by dissolving palladium nitrate hydrate (Strem Chemicals) in 2M nitric acid.

Equal volumes (20 mL) of a chloroform solution of the extractant ($10^{-3}$ or $2x10^{-3}$M according to the stoichiometry of the reaction) and of the aqueous palladium nitrate ($10^{-3}$M) solution were introduced into a stoppered 100 mL glass cylindrical tube which was then shaken for 2 hr on 100 strokes/min at 25°C in an instrument built in these laboratories. For DHS, a 10 hr period of shaking was long enough to establish the equilibrium between the two phases. The mixture was then allowed to stand for 30 min in order to complete the phase separation and the palladium concentration in the aqueous phase was determined by atomic absorption spectrophotometry.

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