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Palladium(II) Extraction by 4-[(Hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole from Hydrochloric Acid Solutions

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Abstract—Palladium(II) extraction from hydrochloric acid solutions by 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole, a new complexing reagent dissolved in toluene or chloroform, was studied. The reagent showed high efficiency in palladium(II) recovery from 0.1–(5–6) M HCl. Palladium(II) is recovered from 1 M HCl by the nonprotonated reagent species according to the coordination mechanism to form the extracted compound $[PdCl_2\mu\text{-}L]_n$ ($n > 2$). The reagent is coordinated to metal ions via the nitrogen atom and the thioether sulfur atom as shown by ^1H and ^{13}C NMR spectroscopy. In the temperature range 10–40°C, palladium(II) extraction from 1 M HCl is an endothermic process. The palladium(II) can be quantitatively stripped by a hydrochloric acid solution of thiourea. The reagent (with toluene as diluent) may be recommended for use in palladium(II) concentration from hydrochloric acid solutions and for palladium(II) selective separation from platinum(IV), copper(II), nickel(II), iron(III), and aluminum(III).

Keywords: 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole, hydrochloric acid
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INTRODUCTION

Large-scale dialkyl sulfide extractants have found application in the production of platinum-group metals (PGMs) for the selective separation of palladium(II) from other PGMs and from associated nonprecious metals via extraction from hydrochloric acid solutions of PGM concentrates [1]. The major disadvantage of dialkyl sulfides consists of low palladium(II) extraction rate [2, 3].

Paiva [4] gives a critical overview of large-scale extractants and those synthesized during the last decade as applied to the selective recovery of palladium(II) from hydrochloric acid solutions of secondary raw material processing (spent industrial and automotive catalysts). Paiva mentions the topicality of syntheses targeted at preparing highly efficient and selective extractants for recovering palladium(II) from such solutions, which considerably differ from PGM concentrate processing solutions by their compositions and lower PGM concentrations. Some new extractants having thioether groups show promise for use in selectively recovering low palladium(II) concentrations, namely, SCS pincer ligands 1,3-bis[2-(octylthio)propan-2-yl]benzene and 1,3-bis[(octylthio)methyl]benzene [5]; calix[*n*]arenes ($n = 4, 6$) functionalized with alkylthiomethyl groups at the upper rim [3]; some *N,N*-dialkyl-substituted monoamides and *N,N,N',N'*-tetraalkyl-substituted diamides functionalized by aliphatic thioether groups [4, 6, 7]. Polydentate calix[*n*]arene thioethers and pincer type extractants far more efficiently and more rapidly extract palladium(II) than dialkyl sulfides [3, 5].

Aminosulfide extractants have higher efficiency compared to that of dialkyl sulfides in palladium(II) recovery from hydrochloric acid solutions due to another extraction stoichiometry. Sufficiently high extraction rates of these metal ions by aminosulfides are due to a rapid phase transfer of anionic chloro complexes of palladium(II) to the organic phase by protonated extractant species [2, 8–10]. The selectivity toward palladium(II) relative to platinum(IV), iridium(IV), and rhodium(III) is not high for aminosulfides having aliphatic or alicyclic (piperidine) amino groups [2, 11]. Far higher palladium(II) recovery selectivity is observed for aminosulfides having weakly basic *N*-containing aromatic heterocycles, such as 2-dodecylthiomethylpyridine [8], 1,2-bis[(5-methyl-1,3,4-thiadiazol-2-yl)thio]ethane [9], and 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole [10].

We showed [10] that 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole (dissolved in chloroform) rapidly (in 5–20 min) and efficiently extracts palladium(II) from 0.1–4 M HCl and has good palladium(II) selectivity relative to platinum(IV) [10]. When an aliphatic or an aromatic diluent ordinary for extraction technology [12] is used, however, a third phase appears during palladium(II) extraction by this reagent, and this circumstance can limit the usefulness of the reagent. In this context it is of interest to study the extraction properties of 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole, a new compound that we synthesized; this compound has an aromatic substituent in the pyrazole ring and allowing toluene to be used as diluent in palladium(II) extraction.

Here, we present the results of a study of palladium(II) extraction by 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole (in toluene or chloroform) from hydrochloric acid solutions.

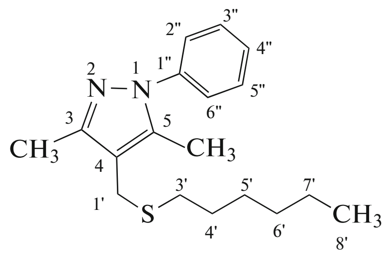
EXPERIMENTAL

The solvents used were: toluene (analytical reagent grade) and chloroform and hexane (both of reagent grade). Aqueous solutions of metal salts were prepared using K_2PdCl_4 prepared, as in [13], from $PdCl_2$ (pure grade); $H_2PtCl_6 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ (pure grade); $FeCl_3 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ (analytical reagent grade); $NiCl_2 \cdot 6H_2O$ and HCl (reagent grade); for stripping agent solutions, thiourea (analytical reagent grade) was used.

Palladium(II) and platinum(IV) concentrations in hydrochloric acid solutions were determined spectrophotometrically with tin(II) chloride [14]. The palladium(II) in thiourea back-extracts and the extracted compounds were determined in a similar manner after back-extract aliquots and weighted samples of the compounds were converted to chloride solutions by a known way [14]. Other metal ions in aqueous solutions were determined complexonometrically: Cu(II), Ni(II), and Fe(III) as described in [10] and Al(III) by back-titration with $ZnSO_4$ solution with Xylenol Orange as an indicator [15].

The metal ions concentration in the organic phase was calculated as the difference between the concentrations in the aqueous phase before and after extraction. When hydrochloric acid extraction was studied, its concentration in the organic phase was determined by the two-phase titration of the extract [10].

Metal ions and hydrochloric acid extraction experiments and palladium(II) stripping experiments were carried out in separatory funnels at 21 ± 1°C, the volume aqueous-to-organic phase ratio W : O = 1 : 1, and under vigorous stirring; the diluent was toluene or chloroform. In temperature-dependent palladium(II) extraction experiments, a temperature-controlled separatory funnel was used; the temperature was maintained accurate to ±0.2°C. Hydrochloric acid extraction was studied at a phase contact time of 10 min, which was sufficient for extraction equilibrium to be attained. The phase separation time upon metal and hydrochloric acid extraction and upon palladium(II) stripping was 30–60 s.



4-[(Hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole (L) was prepared by heterocyclization of 3-[(hexylsulfanyl)methyl]pentane-2,4-dione by means of phenylhydrazine in ethanol under heating and then chromatographed on a column with silica gel MN Kieselgel 60 (0.063–0.2 μm) with the use of EtOAc–hexane (1 : 2) eluent [16]; it is a light yellow oil. Its identity was verified by elemental analysis, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy. The spectral characteristics of the reagent correspond to published data [16]; its purity was at least 95% as determined by gas-liquid chromatography and NMR spectroscopy. The reagent was well soluble in acetone, ethanol, chloroform, toluene, and hexane. The solubility of the reagent in water was determined as described in [10]. The reagent concentration in saturated aqueous solution was determined by electronic spectroscopy in water–ethanol (1 : 1) at 254 nm (ε = 13750), the wavelength corresponding to the maximum of a wide *K* absorption band of $\pi \to \pi^*$ transitions in the 1-phenyl-substituted pyrazole ring [17, 18]. The reagent solutions in toluene or chloroform were prepared from exact weights.

Extracted palladium(II) compounds $[PdCl_2\mu\text{-}L]_n$ ($n > 2$) were obtained under the saturation of the organic phase. A solution containing 0.060 mol/L of reagent L in a diluent was in contact with a 0.011 M palladium(II) solution in 1 M HCl at W : O = 7.5 : 1 for 1 h (toluene) or at W : O = 10 : 1 for 1.5 h (chloroform). The compounds were precipitated from saturated extracts, washed with hexane, and then dried in air. Light yellow powders were thus obtained, T_m = 207–208°C (toluene) or T_m = 235–239°C (chloroform). The compounds isolated from toluene and chloroform had identical IR and NMR spectra. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.89 (3H, t, ^3J = 6.9, 8'-CH_3); 1.16–1.48 (6H, m, 5',6',7'-CH_2); 1.48–1.60 (2H, m, 4'-CH_2); 2.14 (3H, s, CH_3C-5); 2.70 (3H, s, CH_3C-3); 2.73–2.80 (2H, m, 3'-CH_2); 3.78–3.88 (2H, m, 1'-CH_2); 7.50–7.80 (5H, m, 2",3",4",5",6"-CH). ^{13}C NMR spectrum, δ, ppm: 11.3 ($\underline{C}H_3$C-5); 13.4 ($\underline{C}H_3$C-3); 14.0 (C-8'); 22.5 (C-7'); 27.7 (C-4'); 28.5 (C-5'); 30.7 (C-1'); 31.2 (C-6'); 34.9 (C-3'); 111.6 (C-4); 129.0 (C-2",6"); 130.1 (C-4"); 129.2 (C-3",5"); 137.4 (C-1"); 143.4 (C-5); 150.0 (C-3).

For $C_{18}H_{26}N_2Cl_2PdS$ anal. calcd., %: Cl, 14.78; Pd, 22.17; S, 6.68.

Found, % (toluene): Cl, 13.44; Pd, 22.14; S, 6.92.

Found, % (chloroform): Cl, 14.59; Pd, 22.61; S, 7.14.

Concentrations of the reagent L and platinum-group metals were spectrophotometrically determined and the electronic absorption spectra of solutions were recorded on a Specord M40 spectrophotometer. The IR spectra were recorded on an IR Prestige-21 spectrophotometer (Shimadzu) in the range 4000–400 cm^{-1} (thin film or Nujol mull). The NMR spectra were recorded on a Bruker Avance III spectrometer (operating frequency was 500.13 MHz for ^1H and 125.76 MHz for ^{13}C); the solvent was $CDCl_3$ and the internal standard was tetramethylsilane. The ^{13}C NMR signals were assigned using ^1H–^{13}C HSQC and HMBC two-dimensional heteronuclear methods. The melting temperatures of compounds were determined on a Boethius hot stage.

RESULTS AND DISCUSSION

The good solubilities of 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole in low-polarity diluents and its low water solubility (0.071 g/L at 26°C) make it usable as an extractant.

The study of hydrochloric acid extraction by 0.030 M solution of reagent L in chloroform showed that this reagent starts recovering the acid at higher aqueous phase acidity (2 M HCl) than 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole does (the extractant concentration was 0.030 mol/L; chloroform), whose degree of protonation is 28 and 91% at the initial acid concentration of 0.1 and 1 mol/L, respectively [10]. The degree of protonation of reagent L is 4, 35, and 65% when the aqueous phase acidity is 2, 4, and 6 mol/L HCl, respectively. This points to a far lower basicity of the reagent that has a phenyl substituent at the atom N(1). A phenyl substituent in the position 1 is known to appreciably reduce the basicity of pyrazole compounds [18, 19]. We have not observed, within the determination error bar, that 0.030 mol/L of reagent L in toluene extracted the acid from 0.1–3 M HCl.

From Fig. 1, it follows that the time of reaching equilibrium in palladium(II) extraction by reagent L (in toluene) from 0.1 M HCl was 40 min, and from 1 or 4 M HCl, 60 min. When the diluent was chloroform, equilibrium of palladium(II) extraction from 0.1, 1 and 4 M HCl under the same conditions was established in 75, 90, and 60 min, respectively. In the range of HCl concentrations studied, palladium(II) is recovered by reagent L (in chloroform) far more slowly than by 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole (in chloroform) [10]. This allows us to suggest the coordination mechanism of palladium(II) extraction by nonprotonated species of reagent L. Reagent L (in chloroform) recovers palladium(II) from 1 and 4 M HCl 1.5 to 2 times more rapidly than complexing extractants N-decylpyrazole or N-benzylpyrazole (in chloroform) from 3.5 M HCl at the same extractant concentration [20].

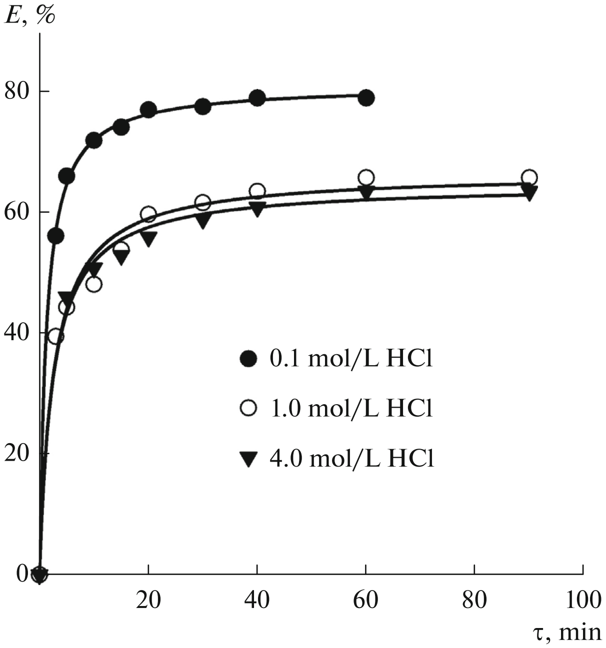


Fig. 1. Kinetic curves of palladium(II) extraction from (C_{HCl} = 0.1 mol/L, C_{Pd} = 0.0056 mol/L; C_{HCl} = 1.0 mol/L, C_{Pd} = 0.0058 mol/L; C_{HCl} = 4.0 mol/L, C_{Pd} = 0.0057 mol/L) by reagent L in toluene (c_L = 0.0040 mol/L).

In 0.1 M HCl, the major palladium(II) species are $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$; when the aqueous phase acidity is 1 mol/L HCl or higher, palladium(II) exists as $[PdCl_4]^{2-}$ [14]. Inner-sphere water molecules in palladium(II) complexes are substituted by neutral ligands, specifically, by pyrazole, more rapidly than chloride ions are [21]. This can be responsible for the more rapid acquisition of equilibrium in palladium(II) extraction by reagent L from 0.1 M HCl (Fig. 1), just as in extraction by tebuconazole (in chloroform) [22], *p*-tolyl(thiomethyl)calix[4]arene (in toluene) [3], or 2-dodecylthiomethylpyridine (in chloroform) [8]. An acceleration of palladium(II) recovery by reagent L (in chloroform) in going to 4 M HCl is likely to arise from the $[PdCl_4]^{2-}$ transfer to the organic phase catalyzed by protonated reagent species, this phase-transfer catalysis being typical of extraction by protonatable aminosulfides [2, 10].

Figure 2 shows the palladium(II), platinum(IV), and iron(III) recovery from individual solutions by reagent L (in toluene) plotted as a function of the initial aqueous hydrochloric acid concentration. Palladium(II) is recovered with high (>99.9%) efficiency from 0.1–5 M HCl. Reagent L in chloroform efficiently (>99.9%) recovers palladium(II) in the concentration range 0.1–6 mol/L HCl under similar conditions with the phase contact time 1.5 h. Palladium(II) can completely be separated from platinum(IV) in the range 0.1–2.5 mol/L HCl; in the range 0.1–3 mol/L HCl, from iron(III) (Fig. 2); and in the range 0.1–6 mol/L

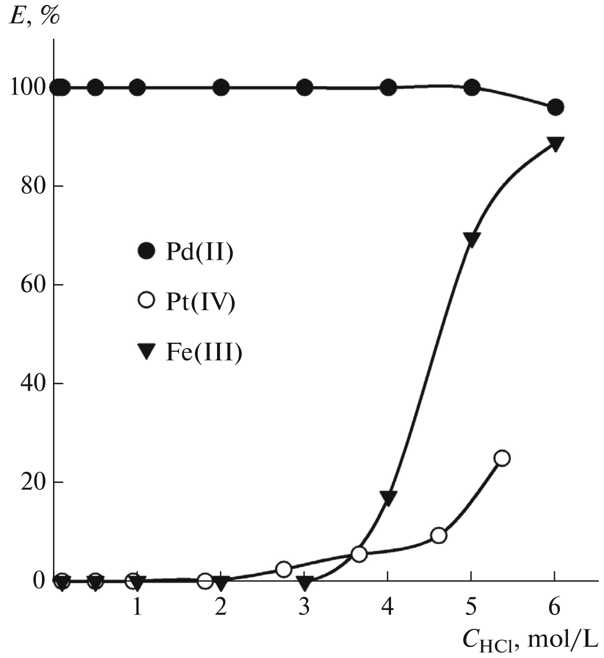


Fig. 2. Palladium(II), platinum(IV), and iron(III) recovery by reagent L (in toluene) versus aqueous HCl concentration (c_{Pd} = 0.0056 mol/L, c_{Pt} = 0.0054 mol/L, c_L = 0.010 mol/L; c_{Fe} = 0.0090 mol/L, c_L = 0.030 mol/L; phase contact time: 1 h).

HCl, from copper(II), nickel(II), and aluminum(III) ($c_{Cu, Ni, Al}$ = 0.010 mol/L; c_L = 0.030 mol/L (in toluene), contact time: 1 h); those metals are not extractable under these conditions. The discovered high selectivity of reagent L in toluene with respect to palladium(II) compared to associated Pt(IV), Cu(II), Ni(II), Fe(III), and Al(III) in the aforementioned acid concentration ranges is commensurate to the selectivities of dialkyl sulfides [23]. When the aqueous phase acidity is 2.7–5.0 mol/L HCl, the palladium(II) distribution ratios (D_{Pd} ~ 10^3) are appreciably higher than platinum(IV) distribution ratios (D_{Pt} = 0.03–0.30), so these elements can be separated with good selectivity. Iron(III) is recovered by reagent L in the form of ion associates L · $HFeCl_4$, as evidenced by the presence of strong absorption bands peaking at 316 and 367 nm that relate to ligand-to-metal charge transfer in the $FeCl_4^-$ tetrahedral ion (T_d), in the electronic absorption spectra of iron(III) extracts obtained at 5–6 M HCl acidities [22].

The effect of some factors on palladium(II) recovery from hydrochloric acid solutions by 0.0050 M solution of reagent L in toluene or chloroform (C_L = 0.0050 mol/L) was studied under equilibrium conditions. At the ionic strength of solution maintained at I = 2 mol/L (HCl + NaCl; c_{Pd} = 0.0055 mol/L), the palladium(II) distribution ratio was found to only weakly depend on hydrogen ion concentration in the range 0.1–2 g-ion/L: the slope of the linear $\log D_{Pd}$–$\log[H^+]$ plot (with toluene as diluent) is 0.30. This value can be a signature of the participation of nonprotonated reagent L in inner-sphere ligand substitution in $[PdCl_4]^{2-}$. An increase in sodium chloride concentration from 0 to 3 mol/L at an aqueous phase acidity of 1 mol/L HCl was accompanied with a decrease in palladium(II) distribution ratio from 7.2 to 3.9 (c_{Pd} = 0.0055 mol/L; diluent: toluene), a trend typical of the coordination mechanism of palladium(II) extraction by neutral extraction agents [23].

The high slopes of palladium(II) extraction isotherms at 1 M HCl (Fig. 3) signify a high efficiency of the extraction agent. The palladium(II) solvate numbers determined by the saturation method are unity, and this indicates that the extracted compounds have the Pd : L = 1 : 1 stoichiometry regardless of the diluent used. The less efficient palladium(II) extraction by reagent L in chloroform is likely due to the blocking of the electron-donating atom N(2) via hydrogen bonding with the proton-donating diluent [24] and the associated additional energy consumption in complexation. Under equal concentration conditions (c_{Pd} = 0.0055 mol/L, 0.0050 mol/L of the extraction agent, and W : O = 1 : 1), the efficiency of equilibrium palladium(II) extraction from 1 M HCl decreases in the following order: 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole in chloroform (contact time: 5 min, D_{Pd} = 9.1) [10] > reagent L in toluene (1 h, D_{Pd} = 5.6) > reagent L in chloroform (1.5 h, D_{Pd} = 3.4). The lower efficiency of reagent L compared to 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole in the same diluent is likely to arise from the nonoccurrence of $[PdCl_4]^{2-}$ phase transfer catalyzed by protonated reagent species, solvation of the reagent by the proton-donating diluent to form a hydrogen bond, and steric hindrances created by the phenyl substituent.

Figure 4 shows that the palladium(II) distribution ratio increases as temperature rises in the range 10–40°C. So, palladium(II) extraction from 1 M HCl is an endothermic process (just as palladium(II) extraction by dialkyl sulfides from hydrochloric acid solutions [23]). Regardless of the solvent used, temperature dependences of distribution ratio have the same slope, and the palladium(II) recoveries feature the same enthalpy change ΔH. This allows us to suggest that the different palladium(II) extraction efficiencies for the diluents used (Figs. 3, 4) are due to the entropy factor.

In order to support the coordination mechanism suggested for palladium(II) extraction, we studied the extracted palladium(II) compounds isolated from extracts saturated at an aqueous phase acidity of 1 mol/L HCl (the diluent was toluene or chloroform) using elemental analysis, electronic absorption spectroscopy, IR and NMR spectroscopy. The compounds isolated from both diluents had the same elemental composition and identical spectral characteristics. They were

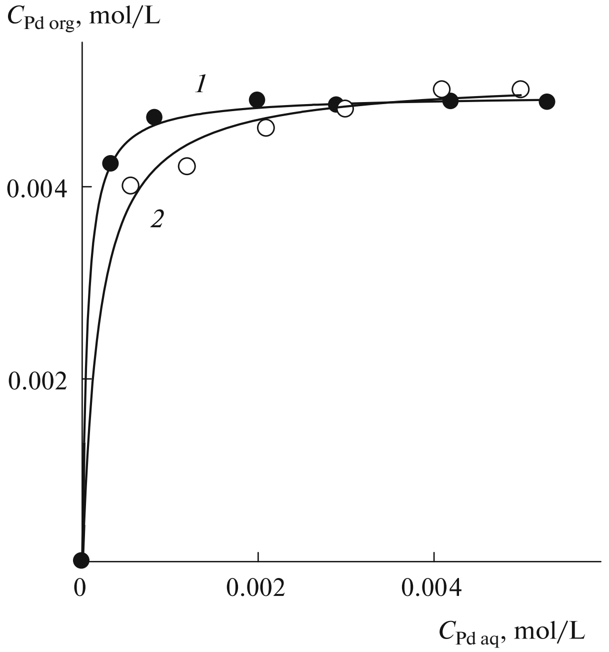


Fig. 3. Palladium(II) extraction isotherms from 1 M HCl by reagent L (c_L = 0.0050 mol/L) in (*1*) toluene, contact time: 1 h; and (*2*) chloroform, contact time: 1.5 h.

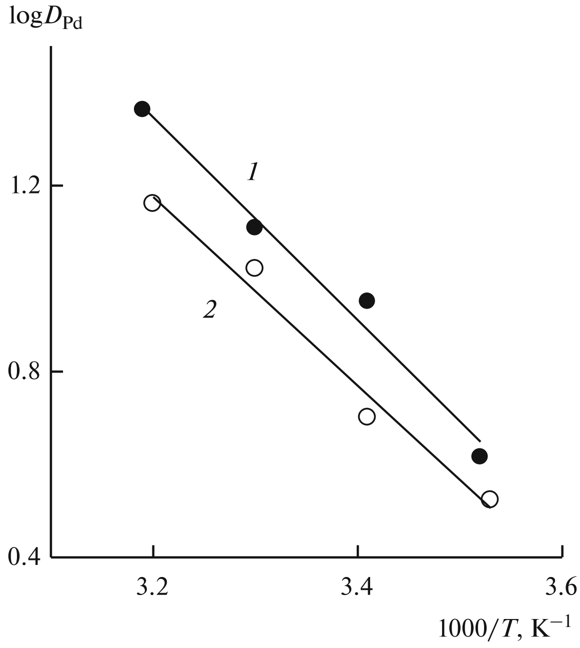


Fig. 4. Palladium(II) distribution ratio versus temperature at aqueous phase acidity of 1 M HCl (c_L = 0.0050 mol/L) where (*1*) the diluent is toluene, c_{Pd} = 0.0046 mol/L, contact time: 1 h; and (*2*) the diluent is chloroform, c_{Pd} = 0.0043 mol/L, contact time: 1.5 h.

well soluble in toluene, chloroform, and acetone; poorly soluble in ethanol and acetonitrile; and insoluble in hexane and water. The Pd, Cl, and S contents in the extracted compounds correspond to the formula unit $PdCl_2L$ and the Pd : L = 1 : 1 stoichiometry, correlating with the solvate number. The absence in the IR spectra (Nujol mulls) of absorption bands due to $N-H^+$ stretching vibrations (in the range 2600–2500 cm^{-1} [10]) and the absence of the 2-NH proton signal in ^1H NMR spectra are indicative of the nonoccurrence of reagent protonation and thereby the absence of ionic associates. In the electronic absorption spectra of the solutions of the compounds in chloroform recorded relative to a solution of reagent L, there are strong absorption band peaking at 239 nm (ε = 13400) relating to Cl → Pd charge transfer, two less strong L → Pd charge-transfer absorption bands at 289 nm (ε = 4700) and 316 nm (shoulder, ε ~ 3600), and a weak absorption band peaking at 426 nm (ε = 306) corresponding to *d–d* transitions in the palladium(II) ion. The spectra of the compounds are similar to the spectra of square-planar palladium(II) complexes with dialkyl sulfides of the type $[PdCl_2L_2]$ [2, 25], and are close to the spectrum of $[PdCl_2\mu\text{-}L]_n$ extracted compound ($n > 2$, L = 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole) [10]. Likely, reagent L, just as 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole, too, is bridging in the extracted compounds, and the compounds are polymeric complexes $[PdCl_2\mu\text{-}L]_n$ ($n > 2$) with $PdCl_2N_2$ and $PdCl_2S_2$ coordination cores (N and S are the donor atoms of the reagent). In the visible wavelength range, the spectra of extracts obtained after recovery of palladium(II) by reagent L (in toluene or chloroform) from 0.1–4 M HCl, also feature an absorption band (shoulder) of *d–d* transitions in the complex peaking at about 420 nm (the spectra were recorded relative to the diluent).

In order to elucidate in which mode reagent L is coordinated to palladium(II) ions, we considered the ^1H and ^{13}C NMR spectra of the extracted compounds as compared to the earlier published respective spectra of reagent L [16]. In the ^1H NMR spectrum of reagent L, the singlet proton signals from 5-CH_3 and 3-CH_3 methyl groups appear at 2.27 and 2.31 ppm, respectively. In the spectra of extracted compounds, the singlet from 5-CH_3 protons shifts by 0.13 ppm to high fields and the signals from 3-CH_3 protons shift by 0.39 ppm to low fields. The considerable deshielding of 3-CH_3 protons is likely to arise from the coordination of the reagent via the atom N(2) of the pyrazole ring. In the ^{13}C NMR spectra of the extracted compounds, the CH_3C-3 methyl carbon signal experiences a far greater low-field shift (the chemical shift change relative to the signal of the respective atom in the reagent spectrum is Δδ = 1.7 ppm) than the CH_3C-5 methyl carbon signal (Δδ = 0.2 ppm); this supports the suggested coordination of the reagent via the atom N(2). The chemical shifts of the signals of C-4, C-5, and C-3 carbon atoms (appearing at 111.6, 143.4, and 150.0 ppm, respectively) and those of the carbon atoms from CH_3C-5 and CH_3C-3 methyl substituents (at 11.3 and 13.4 ppm, respectively) are close to the chemical shifts of the signals of the respective atoms in the 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole coordinated to the palladium(II) atom via the atom N(2) in the ^{13}C NMR spectrum of the palladium(II) chloro complex with this ligand: $[PdCl_2\mu\text{-}L]_n$ ($n > 2$) [10].

In the ^1H NMR spectrum of reagent L, proton signals from the 3'-CH_2 and 1'-CH_2 methylene groups of the hexylsulfanylmethyl substituent appear at 2.49 ppm (t) and 3.58 (s) ppm, respectively. In the spectra of extracted compounds, multiplet signals in the range 2.73–2.80 and 3.78–3.88 ppm correspond to the 3'-CH_2 and 1'-CH_2 nonequivalent protons, respectively. A considerable low-field shift of proton signals from the 3'-CH_2 ($\Delta\delta = 0.28$ ppm) and 1'-CH_2 ($\Delta\delta = 0.25$ ppm) methylene groups, which are adjacent to the sulfur atom, and the nonequivalence of protons in these groups can arise from the coordination of the reagent via this heteroatom [10, 25]. The ^{13}C NMR spectra of extracted compounds feature the greatest chemical shift changes for the signals from the C-1' ($\Delta\delta = 5.5$ ppm) and C-3' ($\Delta\delta = 2.9$ ppm) carbon atoms of the thioether substituent; this feature indicates that the reagent is coordinated via the sulfur atom.

Thus, NMR spectroscopic data allow us to infer that reagent L in extracted compounds is coordinated to palladium(II) ions via the electron-donating sulfur and nitrogen N(2) atoms.

The results of above-described studies show that 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole in toluene or chloroform extracts palladium(II) by a coordination mechanism and, unlike in extraction by 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1*H*-pyrazole, which has a higher basicity, the stage of rapid $[PdCl_4]^{2-}$ transfer to the organic phase catalyzed by the protonated reagent species can be avoided.

The opportunity of quantitative palladium(II) stripping makes it possible to use the extractant in the extraction–stripping cyclic mode. Upon two cycles comprising the stages of palladium(II) extraction from 1 M HCl ($c_{Pd} = 0.0056$ mol/L, $c_L = 0.010$ mol/L, toluene, contact time: 1 h), palladium(II) stripping by 0.1 mol/L thiourea in 0.1 M HCl (contact time: 15 min), and washing of the extractant with 1 M HCl (W : O = 1 : 1, contact time 3 min), the palladium(II) recovery was greater than 99.9% and the stripping was 98% in each cycle.

The high efficiency of reagent L makes it useful for concentrating palladium(II) with a small overstoichiometric excess of the reagent. Tenfold palladium(II) concentration from 1 M HCl with the complete (>99.9%) palladium(II) recovery to the organic phase was shown to be feasible ($c_{Pd} = 0.0043$ mol/L, $c_L = 0.060$ mol/L, diluent: toluene, W : O = 10 : 1, contact time: 1 h). A small excess of the reagent appreciably accelerates quantitative palladium(II) recovery; a 0.015 M solution of reagent L in toluene at W : O = 1 : 1 provides the complete recovery of metal ions from the solution containing 0.0055 mol/L palladium(II) to 1 M HCl, in 5 min.

CONCLUSIONS

The new reagent 4-[(hexylsulfanyl)methyl]-3,5-dimethyl-1-phenyl-1*H*-pyrazole in toluene or chloroform is a highly efficient neutral complexing extractant for recovering palladium(II) from hydrochloric acid solutions (0.1–(5–6) M HCl) with a moderate salt background.

Reagent L in toluene shows promise for use in the concentration and highly selective separation of palladium(II) from Pt(IV), Cu(II), Ni(II), Fe(III), and Al(III) via extraction from hydrochloric acid solutions obtained by leaching of secondary raw materials.

The coordination extraction scheme has been proposed for palladium(II) extraction from 1 M HCl by nonprotonated L species in toluene or chloroform to yield $[PdCl_2\mu\text{-}L]_n$ ($n > 2$) extracted compounds, where L is coordinated to metal ions via the electron-donating nitrogen N(2) and thioether sulfur atoms.

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

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