Comparative Studies on the Solvent Extraction of Pd(II) Using Alkane-1,ω-diyl Bis(*O*,*O*-diisobutyl phosphorodithioate)s

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A series of new bis-type derivatives of *O*,*O*-diisobutyl phosphorodithioate, namely, the alkane-1,ω-diyl bis(*O*,*O*-diisobutyl phosphorodithioate)s (ADBDiBPDT), were synthesized for use in the solvent extraction of precious metals. These compounds having the general formula $(i\text{-BuO})_2P(S)S(CH_2)_nS(S)P(Oi\text{-Bu})_2$, have considerable selectivity for extraction of Pd(II) over Au(III), Ag(I), and Pt(IV) when extracted from 0.1 M (1 M = 1 mol dm^{-3}) perchlorate, nitrate, and chloride media. The extractability of individual metal ions increases with the increase in the length of the alkane-1,ω-diyl chain ($n = 1$—4), joining the two phosphorodithioate groups in the bis-structure. The extraction of palladium(II) from 1.0 M chloride solution at pH 3 in 1,2-dichloroethane (DCE) proceeds through the formation of either a 1 : 2 ($n = 1$) or a 1 : 1 ($n = 2,3,4$) palladium-ligand complex involving ligand displacement in $PdCl_4^{2-}$ species. When compared with the monofunctional triisobutylphosphine sulfide (TIBPS) and dihexyl sulfide (DHS), the new reagents were found to provide higher Pd(II) extraction and better extraction selectivity, under identical conditions. The higher members of the ADBDiBPDT series acting as bidentate ligands are also characterized by better stripping properties compared with those of the monodentate sulfur ligands. The metal loading capability, the extraction constants, and the kinetic properties of palladium extraction using these reagents are discussed.

O,*O*-Dialky and *O*,*O*-diaryl phosphorodithioates have been studied extensively in the past as extractants for various metal ions.[1] These reagents extract metal ions through formation of strong chelates of the type $(G_2P:SS^-)_nM$ (G = an alkoxy or aryloxy group; M = a metal ion), where considerable selectivity towards soft metal cations is observed. In a systematic investigation[2] on the extraction with *O*,*O*-dibutyl phosphorodithioate in carbon tetrachloride, the displacement order for metal ions was found to be: Pd(II) > Au(III) > Cu(I) > Hg(II) > Ag(I) > Cu(II) > Sb(III) > Bi(III) > Pb(II) > Cd(II) > Ni(II) > Zn(II). Both the *O*,*O*-diethyl and *O*,*O*-dibutyl derivatives of phosphorodithioate provided quantitative extraction of palladium, silver, gold, and copper from a wide range of acidity in HCl or H_2SO_4 media.[2—4] In spite of the high extraction capabilities and wider range of operational acidity, the *O*,*O*-dialkyl phosphorodithioates or their metal salts have not found acceptance in analytical or industrial use for solvent extraction. This is because of the fact that these reagents are rather unstable and water-soluble. Back-extraction of the metal ions from the organic phase is often difficult due to very strong chelation involving the thiolo sulfur atom. In a recent study on the extraction of Ag with *O*,*O*-dialky phosphonothioates and phosphonodithioates (cyanex 301 and cyanex 302), we envisaged that the non-destructive stripping of the metal would be extremely difficult.[5] The situation may be more rigorous in the case of palladium since it has a higher cationic charge and smaller ionic radius. In view of these points, it will be interesting to synthesize neutral bis-derivatives of *O*,*O*-dialkyl phosphorodithioates for the extraction of Pd(II), where the problem of inner coordination is completely avoided. Moreover, the distribution of donor atoms in the ligand chain can effectively be modified to construct useful cavity structures leading to improved selectivity for a particular metal cation.

Based on the assumed advantages of the bis-type sulfur ligands, we reported the extraction of Pd(II) and Ag(I) with alkane-1,ω-diyl bis(*O*-butyl dithiocarbonate)s.[6,7] In the case of palladium, the extraction process was found to be favorable regarding the equilibrium parameters, extraction kinetics, and selectivity considerations. But, quantitative back-extraction of Pd was possible only with multiple-stage stripping using thiourea as the reagent. The aim of this work was to synthesize new bis-type compounds based on *O*,*O*-dialkyl phosphorodithioates for the study of Pd(II) extraction. In the last 10—15 years, a large number of neutral sulfur compounds have been introduced as extractants for palladium, but only a few have developed industrial importance. The slow kinetics of extraction and the lack of appropriate selectivity amongst the precious metal ions, as are inherent in most sulfur ligands, may probably be blamed for their limited applications. In this respect, the development of new extractant systems is essential to facilitate the recovery of precious metals from indigenous sources as well as to improve our knowledge about precious metal chemistry.[8] In this paper, new type of phosphorodithioate derivatives namely, the alkane-1,ω-diyl bis(dialkyl phosphorodithioate)s are described as extractants for Pd(II). The new compounds are compared with two widely known monofunctional sulfur reagents, dihexyl sulfide[9] and triisobutylphosphine sulfide,[10] in terms of the extraction equilibria, selectivity, back-extraction, and kinetic considerations.

Experimental

Extractants Alkane-1,*ω*-diyl bis(*O*,*O*-diisobutyl phosphorodithioate)s were synthesized using a two-step procedure as described in the following.

2-Methyl-1-propanol (0.500 mol) was heated to 60 °C a in a 500 mL conical flack and was kept under vigorous stirring. Diphosphorus pentasulfide (0.125 mol) was added to the alcohol in 10-g portions, at intervals of 15 min. At the end of P_2S_5 addition, the flask was fitted with a refluxing condenser and the reaction was maintained for 4 h at 60—70 °C. After quick cooling and leaving overnight, a blue-black solution of *O*,*O*-diisobutyl phosphorodithioate was formed. It was filtered to remove the suspended solids and warmed to 60 °C in a glass tube. Gaseous ammonia was bubbled from the bottom until the mixture became alkaline to litmus paper. The crystals of ammonium *O*,*O*-diisobutyl phosphorodithioate were dried using a rotary evaporator and recrystallized from a 1 : 1 benzene–ethanol mixture. Colorless crystals, mp 128—130 °C. Yield, 82%. Found: C, 37.32; H, 8.48; N, 5.37%. Calcd for $C_8H_{22}NO_2PS_2$: C, 37.05; H, 8.55; N,5.40%. ^{1}H NMR data, δ (ppm) = 0.97 (d, 12H, CH_3–), 1.96 (m, 2H, $\rangle$CH–), 3.77 (t, 4H, –O–CH_2–), 6.34 (br, 4H, NH_4). The ^{1}H NMR of the compounds reported in this paper were recorded in $CDCl_3$ using TMS as the internal standard and the splitting of the signals are expressed as, s: singlet, d: doublet, t: triplet, m: multiplet, and dt: double triplet.

In step 2, ammonium *O*,*O*-diisobutyl phosphorodithioate (0.03 mol), as obtained above, was dissolved in 100 mL of acetone in a four-neck flask. The solution was heated to reflux with continuous stirring of the contents. Solution (15 mL) of the selected 1,*ω*-dibromoalkane (0.015 mol) in the same solvent was dropped slowly into the flask and the reaction conditions were maintained for 1 h. The mixture was cooled overnight and filtered to remove the white mass of the NH_4Br. Evaporation of the solvent acetone provided the crude product of the bis-compound as an oily liquid and was purified by flash chromatography. The synthesized ligands were analyzed for their composition and structure by using elemental analysis, ^{1}H NMR, and FTIR data.

Methylene bis(*O*,*O*- diisobutyl phosphorodithioate), MBDiBPDT. Found: C, 41.26, H, 7.50%. Calcd for $C_{17}H_{38}O_4P_2S_5$: C, 41.11; H, 7.71%. ^{1}H NMR δ = 0.98 (d, 24H, CH_3–), 2.03 (m, 4H, $\rangle$CH–), 3.91 (m, 8H, –O–CH_2–), 4.28 (t, 2H, –S–CH_2–S–). IR 667 cm^{-1}, ν(P=S).

Ethylene bis(*O*,*O*-diisobutyl phosphorodithioate), EBDiBPDT. Found: C, 41.40; H, 7.54%. Calcd for $C_{18}H_{40}O_4P_2S_4$: C, 42.33; H, 7.54%. ^{1}H NMR δ = 0.97 (d, 24H, CH_3–), 2.05 (m, 4H, $\rangle$CH–), 3.17 (d, 4H, –S–CH_2–), 3.88 (dt, 8H, –O–CH_2–). IR 671 cm^{-1}, ν(P=S).

Trimethylene bis(*O*,*O*-diisobutyl phosphorodithioate), TrMBDiBPDT. Found: C, 42.87; H, 7.97%. Calcd for $C_{19}H_{42}O_4P_2S_4$: C, 43.49; H, 8.07%. ^{1}H NMR δ = 0.97 (d, 24H, CH_3–), 2.01 (m, 4H, $\rangle$CH–), 2.07 (m, 2H, S–C–CH_2–C–S); 2.99 (m, 4H, –S–CH_2–); 3.87 (dt, 8H, –O–CH_2–). IR 673 cm^{-1}, ν(P=S).

Tetramethylene bis(*O*,*O*-diisobutyl phosphorodithioate), TtMBDiBPDT. Found: C, 44.05; H, 7.99%. Calcd for $C_{20}H_{44}O_4P_2S_4$: C, 44.59; H, 8.23%. ^{1}H NMR δ = 0.97 (d, 24H, CH_3–), 1.81 (m, 4H, S–C–CH_2–), 1.99 (m, $\rangle$CH–), 2.92 (d, 4H, –S–CH_2–), 3.84 (dt, 8H, –O–CH_2–). IR 675 cm^{-1}, ν(P=S).

Triisobutylphosphine sulfide, TIBPS, was obtained in the pure form by recrystallization of the crude product (CYANEX 471X), as kindly supplied by Cytec Canada Inc.

Dihexyl sulfide, DHS, as obtained from Daihachi Chemical Industry Co., Ltd., Tokyo was of 99% purity and was used without further purification.

Chemicals. Stock solutions (0.1 mol dm^{-3}) for Pd(II) and Pt(IV) were prepared by dissolving $PdCl_2$ and $H_2PtCl_6 \cdot 6H_2O$ in 0.1 mol dm^{-3}hydrochloric acid. $AgNO_3$ was dissolved in water to obtain the silver stock solution, and working solutions for Au(III) were prepared from 1000 ppm AAS standard solution ($HAuCl_4$ in 1 mol dm^{-3} HCl). Diphosphorus pentasulfide used in the synthesis of the ligands was 97% pure. Other chemicals were of at least A.R. grade purity. Distilled and de-ionized water was used throughout. All experiments were done at ambient temperatures (25±2°C). 1,2-Dichloroethane (DCE), used as the diluent, was saturated with water before use in the extraction experiments.

Solvent Extraction Procedures. A 10-mL portion of the aqueous metal ion solution in the appropriate medium was shaken horizontally in a glass-stoppered tube with an equal volume of the ligand solution in DCE for a predetermined time. The shaking speed was fixed at 300 oscillations per min using a Hirasawa Shaker Model SH-S1. After phase separation, the metal ion concentration in the aqueous phase was measured by using atomic absorption spectrometry (AAS) (Seiko SAS 7500 A). The distribution ratio of the metal ion was evaluated by computing the organic phase concentration from the mass balance before and after equilibration. In some samples, where the equilibrium metal ion concentrations in the aqueous phase approached the detection limit of the measuring system, the organic phase was analyzed directly in the AAS, the concentration values being corrected for the difference of density between the aqueous standard solution and the metal-loaded organic phase solutions.

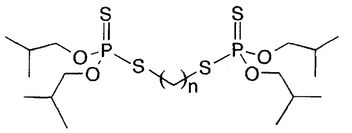
A back-extraction experiment was done in a manner similar to the extraction experiment, where the organic phase concentration of palladium was used to calculate the percent stripping of the metal.

The distribution constant (K_{DR}) values of the extractants between DCE and 0.1 mol dm^{-3} HCl were calculated by following a procedure adopted by Ohashi etal.[11] A solution (25 mL) of the ligand in DCE was equilibrated with 280 mL of 0.1 mol dm^{-3} of aqueous hydrochloric acid for 4 h in a separatory funnel. After phase separation, 200 mL of the aqueous phase was transferred to another funnel and extracted with 20 mL of fresh DCE by shaking vigorously for 5 min. The distribution constant was evaluated by measuring the concentration of the ligand in both phases spectrophotometrically (λ_{max} around 225 nm).

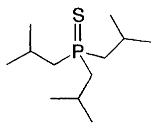
Results and Discussion

Properties of Alkane-1,*ω*-diyl Bis(*O*,*O*-diisobutyl phosphorodithioate)s. Table 1 lists the general structure, composition, and some physical properties of the synthetic reagents. From the general structure, it can be seen that each ligand contains two sulfide (P–S–C) and two thiono (P=S) sulfur atoms that can be used by these compounds to coordinate with metal ions. It is well established that a thiono sulfur has much less coordinating ability than a sulfide sulfur.[12] Moreover, the phosphorus atoms in the bis-molecule are attached directly to two oxygen atoms, dragging the electron density away from the P=S bond. The possible coordination of the alkane-1,*ω*-diyl bis(*O*,*O*-diisobutyl phosphorodithioate)s with soft metal ions would thus

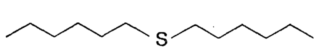
Table 1. General Structure, Composition, and Properties of the Ligands under Study



(ADBDiBPDT)



(TIBPS)



(DHS)

n	Ligand	Physical state	Mp/bp °C	Specific gravity	K_{DR}[a)]	Yield %
1	Methylene bis(*O*,*O*-diisobutyl phosphorodithioate) (MBDiBPDT)	Colorless liquid	> 200	1.04	4.5×10^{4}	72
2	Ethylene bis(*O*,*O*-diisobutyl phosphorodithioate) (EBDiBPDT)	Colorless liquid	> 200	1.06	2.5×10^{4}	79
3	Trimethylene bis(*O*,*O*-diisobutyl phosphorodithioate) (TrMBDiBPDT)	Colorless liquid	> 200	1.15	7.1×10^{4}	84
4	Tetramethylene bis(*O*,*O*-diisobutyl phosphorodithioate) (TtMBDiBPDT)	Colorless liquid	> 200	1.16	4.1×10^{4}	86
	Triisobutylphosphine sulfide (TIBPS)[b)]	Crystalline solid	58—59	0.91	1.8×10^{5}	—
	Dihexyl sulfide (DHS)[b)]	Colorless liquid	—	0.81	3.8×10^{5}	—

a) The K_{DR} values refer to the distribution of the ligand between its DCE solution (1×10^{-1} to 1×10^{-3} M) and 1×10^{-1} M aqueous HCl solution. b) Data are quoted either from the literature or from manufacturer's catalog.

involve the sulfide sulfurs in the molecule. Since the two sulfide sulfur are situated at equivalent positions in the ligand skeleton, a bifunctional interaction would be more favorable for these ligands, if steric requirements are satisfied. Regarding physical properties, the ADBDiBPDTs are found to be high boiling liquids with specific gravity values just above 1; signifying that the compounds are suitable as good extractants in liquid–liquid separations of metal ions.[13)] The aqueous phase immiscibilities of the bis-compounds, as expressed by the K_{DR} values in Table 1, are on the order of 10^4, roughly an order less in magnitude compared to those of monofunctional TIBPS or DHS, yet they can be considered as highly acceptable for being used in solvent extraction.[14)]

Extraction of Precious Metals with ADBDiBPDTs and Comparison with Monofunctional Reagents. To evaluate the usefulness of the newly synthesized alkane-1,ω-diyl bis(*O*,*O*-diisobutyl phosphorodithioate)s in precious metal recovery, their extracting capabilities for Au^{3+}, Pd^{2+}, Ag^{+}, and Pt^{4+} were measured in aqueous perchlorate, chloride, and nitrate media. The extracting capability of TIBPS and DHS was also measured in a similar way. The results are compared in Table 2. In general, the data show that the extracting power of ADBDiBPDTs for a particular metal ion increases with the increase in the length of the carbon chain separating the two phosphorodithioate groups in the ligand molecule. In the extraction of Pd(II) with alkane-1,ω-bis(*O*-butyl dithiocarbonate)s, a separation of a 3-carbon chain between the two coordinating sulfur atoms was found to provide optimum extraction.[6)] These bis-compounds are made from joining two *O*,*O*-diisobutyl phosphorodithioate groups, which are much larger in size than the *O*-butyl dithiocarbonate groups and thus allow much less space for the metal ions to come closer to the coordinating atoms. Therefore, extraction is favored with still greater ($>C_3$) size of the ligand cavity. If we compare the precious metal extractabilities of ADBDiBPDTs with those of TIBPS and DHS, it is seen that the bis-compounds extract Pd(II) more selectively than either of the monodentate ligands. This can be interpreted on the basis of steric requirements of the metal complexes concerned. Pd(II) is known to form exclusively square-planar complexes with sulfur donors.[12)] In such an arrangement, the two sulfide sulfur atoms in a ADBDiBPDT structure can approach the metal ion more closely without suffering much strain along the ligand skeleton. In the formation of a tetrahedral Au(III) or a linear Ag(I) complex, both strain and hindrance along the ligand chain come into effect, making such complexes comparatively less stable. The monofunctional TIBPS and DHS, on the other hand, are free from strain and direction effects, where the metal-ligand coordination is mainly defined by the attraction of the coordinating sulfur for metal ion balanced by the steric hindrance of the ligand structure. This results in a rather poor selectivity to coordination. The Pt(IV) extraction is very small with each of the ligands studied because of the kinetic inertness of the Pt(IV)–sulfur reactions.[15)] Summarizing the results, the order of extractability of metal ions using these ligand systems can be written as, ADBDiBPDT: $Pd^{2+} > Ag^{+} > Au^{3+} > Pt^{4+}$ (except in NO_3^-); TIBPS: $Ag^{+} > Au^{3+} > Pd^{2+} > Pt^{4+}$; DHS: $Au^{3+} > Ag^{+} > Pd^{2+} > Pt^{4+}$.

Pd(II) Extraction Equilibria. The equilibrium of Pd(II) extraction was studied in 1.0 M chloride solutions. This is due to the fact that the practical recovery of palladium is for the most part done in chloride solutions.[8)] From the preliminary studies, it was found that the distribution ratio of palladium, *D*, is independent of the aqueous acid concentration in the pH range 2.0—8.0, when palladium was

Table 2. Extraction of Precious Metal Ions Using Sulfur Ligands from Various Media

Ligand	Extraction of metal ions/%									
	0.1 M $NaClO_4$			0.1 M NaCl			0.1 M $NaNO_3$			
	Pd^{2+}	Ag^+	Au^{3+}	Pd^{2+}	Au^{3+}	Pt^{4+}	Pd^{2+}	Ag^+	Au^{3+}	Pt^{4+}
MBDiBPDT	98.7	30.4	10.8	44.2	16.9	0.0	100	7.5	18.1	1.2
EBDiBPDT	94.7	60.5	18.2	69.9	18.1	0.0	100	17.4	23.6	0.0
TrMBDiBPD	98.4	61.2	15.1	74.2	18.9	0.0	100	17.8	28.6	0.0
TtMBDiBPDT	98.4	63.7	19.7	92.1	20.3	0.1	100	20.5	33.0	0.0
TIBPS	49.1	99.8	97.7	41.6	70.0	1.9	75.1	100	100	2.3
DHS	25.9	30.7	98.9	21.8	85.0	1.5	61.1	82.1	100	1.9

$[M^{n+}]_{Init} = 1.0\times10^{-4}$ M at pH 5.5 (adjusted by small additions of NaOH/corresponding acid); [Ligand] $=2.5\times10^{-3}$ M in DCE; Shaking Time = 1 h; Phase Ratio = 1.

extracted with these ligands from 1.0 M chloride medium. The evaluation of the extraction equilibria was thus done at pH 3.0. In the first place the log D versus log [L] plots were measured for each of the reagents to find out the metal-ligand ratio in the extracted complex. As seen in Fig. 1, the ligand, MBDiBPDT (I, $n=1$) extracts Pd(II) forming a 1 : 2 Pd–MBDiBPDT complex, as estimated from the slope of the concerned curve. The slope values for EBDiBPDT (II, $n=2$), TrMBDiBPDT (III, $n=3$), and TtMBDiBPDT (IV, $n=4$) approach unity in their respective log D–log [L] plots, indicating that a 1 : 1 stoichiometry is true for extraction of Pd(II) with those ligands. Both TIBPS (V) and DHS (VI) are characterized with a 1 : 2 stoichiometry, at lower concentrations of the ligands. At higher concentrations ($>3.2\times10^{-3}$ M), TIBPS shows the tendency to form a 1 : 1 complex, as was also observed in the extraction of the metal from 1 M HCl.[16] However, for comparison in this study, only the lower part of the TIBPS curve was considered.

The stoichiometry of the extracted complex with respect to the chloride composition was also measured by the slope ratio method (Fig. 2). The log D versus log $[Cl^-]$ plot measured with a fixed reagent concentration, produced slope values close to −2, with each of the reagents under study. This would mean that two chloride ions are released from the aqueous chlorocomplex of Pd(II), which is responsible for the reaction with the ligand.

Under these experimental conditions, palladium in the aqueous phase (1.0 M chloride) is expected to exist as the tetrachloro complex, $PdCl_4^{2-}$ accompanied by small amounts of the aquo trichloro complex, $Pd(H_2O)Cl_3^-$ and aquo dichloro complex, $Pd(H_2O)_2Cl_2$.[16,17] Taking into account the coordination number of Pd(II), the overall reaction responsible for the extraction with these ligands can be ex-

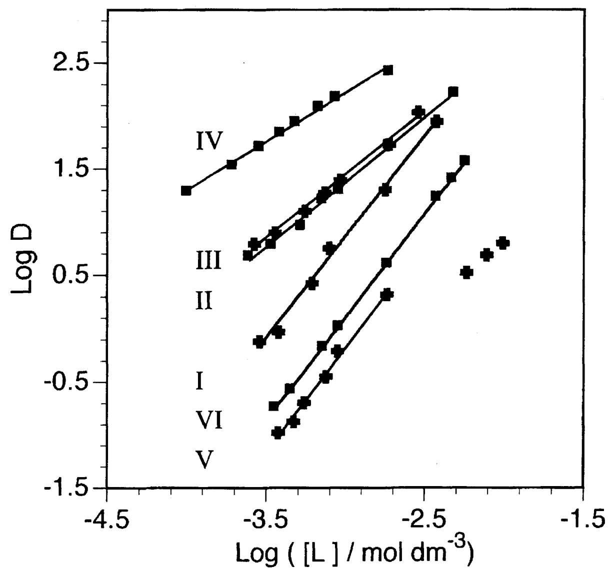


Fig. 1. log D vs. log [L] plots for the extraction of Pd(II) using the reagents under investigation. $[Pd^{2+}]=1\times10^{-4}$ M in 1 M NaCl (pH 3); Shaking Time = 18 h. Description of the curves (number, ligand, slope value): I, MBDiBPDT, 1.89; II, EBDiBPDT, 1.19; III, TrMBDiBPDT, 1.22; IV, TtMBDiBPDT, 0.95; V, TIBPS, 1.95, VI, DHS, 1.93.

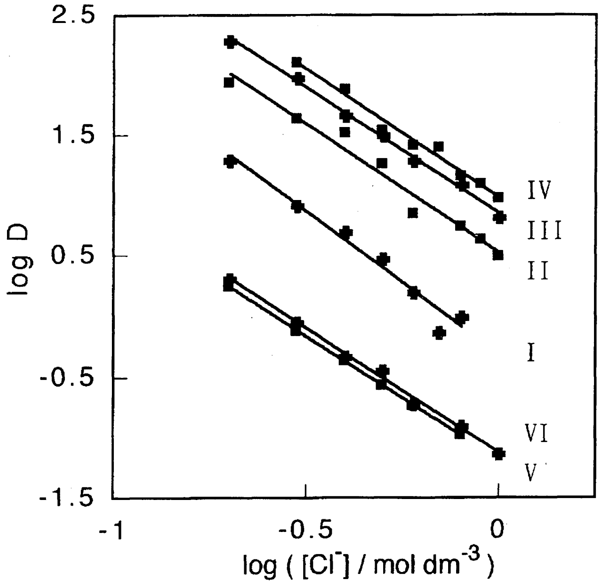


Fig. 2. log D vs. log $[Cl^-]$ plots for the extraction of Pd-(II) using various reagents. [Ligand] $=1\times10^{-3}$ M in DCE; $[Pd^{2+}]=1\times10^{-4}$ M. Shaking Time = 18 h. Curves (number, ligand, slope value): I, MBDiBPDT, −2.36; II, EBDiBPDT, −2.11; III, TrMBDiBPDT, −2.14; IV, TtMB-DiBPDT, −2.14; V, TIBPS, −2.05; VI, DHS, −2.03.

pressed as:

$$\mathrm{PdCl_4}^{2-} + x\overline{\mathrm{L}} \overset{K'_{\mathrm{ex}}}{\rightleftharpoons} \overline{\mathrm{PdL}_x\mathrm{Cl}_2} + 2\mathrm{Cl}^- \qquad (1)$$

or

$$\log K'_{\mathrm{ex}} = \log D + 2\log[\mathrm{Cl}^-] - x\log[\overline{\mathrm{L}}], \qquad (2)$$

where x=2 for the extraction with MBDiBPDT, TIBPS, DHS, and $x=1$ for extraction with EBDiBPDT, TrMBDiBPDT, and TtMBDiBPDT. In Eqs. 1 and 2, K'_{ex} represents the conditional extraction constant of the specified reaction and the overbar refers to the species in the organic phase. It is interesting to find that the MBDiBPDT (n=1) acts as a monodentate ligand towards Pd(II) although it has the same set of donor atoms as the bidentate analogues, EBDiBPDT, TrMBDiBPDT, and TtMBDiBPDT do. The formation of two types of complexes by the ADBDiBPDTs is also supported by the electronic spectra of the Pd(II) complexes of the concerned ligands in DCE. As shown in Fig. 3, the UV-vis spectrum of the Pd(II)-MBDiBPDT (I) complex resembles the spectra of the Pd(II) complexes of the monodentate TIBPS (V) and DHS (VI), with two sharp peaks at 295.0 and 224 nm, respectively. The peaks of TIBPS and DHS complexes appear at 332, 247 and 308, 245 nm, respectively. The Pd(II) complexes of the bidentate EBDiBPDT (II), TrMBDiBPDT (III), and TtMBDiBPDT (IV), on the other hand, produce spectra having a single broad peak at 294, 303, and 300 nm, respectively. Although no attempt was made to take quantitative account of the electronic spectra, it may be assumed that the two spectral patterns for the palladium complexes are obtained because of the proximity of the donor sulfurs in the respective square-planar configuration. In the cases of monodentate coordination, the donors are expected to approach the metal ion from opposite corners of the square, giving a *trans*-configuration to the Pd(II) complex with respect to the two sulfur donors.[18] The bidentate bis-coordination, on the other hand, would result in a *cis*-configuration for the complex owing to the steric constraints in the ligand structure. In the interpretation of the UV-visible spectra of Co(III) complexes, Shimura,[19] following the works of previous researchers, showed that there is always an additional band in the spectra of the *trans*-isomers compared to those of the corresponding *cis*-complexes. Again it was proved by a number of workers that the *trans*-complexes invariably give sharp peaks in their electronic spectra, while the *cis*-complexes are characterized with having broader peaks.[20] The observed number and shape of the UV-vis peaks in the Pd(II) complexes of ADBDiBPDTs are indicative of the presence of two geometrical forms, to be identified as having 1 : 2 or 1 : 1 stoichiometries, in the concerned complexes. The failure of the MBDiBPDT to form a bis-coordinated complex may be attributed to the shorter distance (n=1) between the donor atoms, where the steric hindrance of the large *O*,*O*-

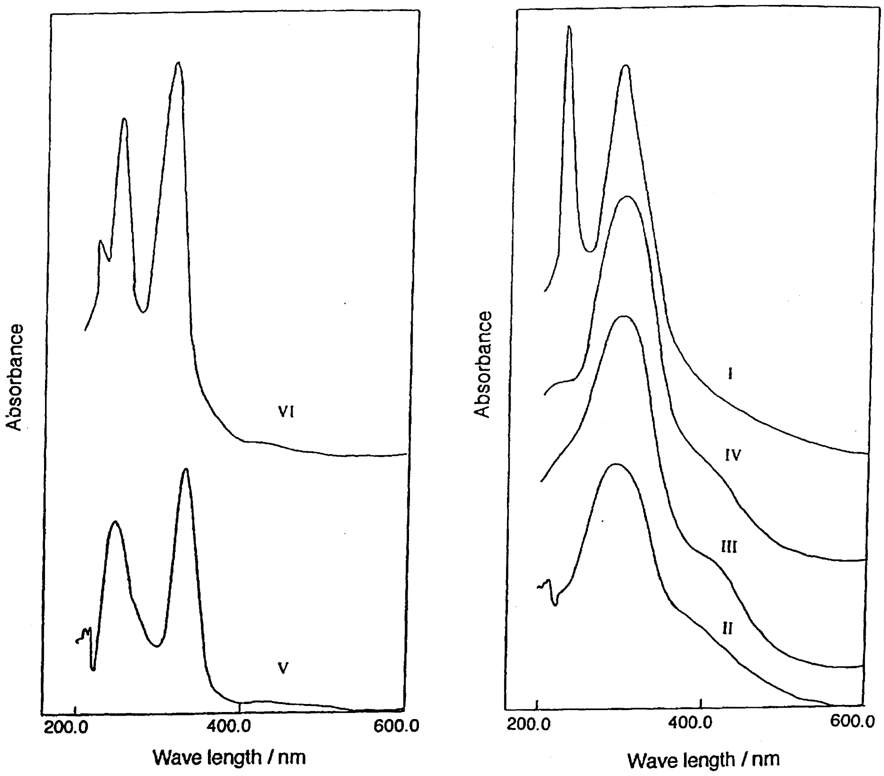


Fig. 3. Electronic spectra of the Pd(II) complexes of the selected ligands. $[\mathrm{PdCl_2L}_x] = 5\times10^{-5}$ M, prepared by equilibrating either 1×10^{-4} (1 : 2) or 5×10^{-5} M (1 : 1) of the ligand solution in DCE with equal volume of 1×10^{-2} M Pd(II) solution in 1.0 M NaCl for 36 h. Spectra of the organic phase were recorded with reference to the corresponding ligand solution as the blank. Curves: I, $\mathrm{Pd(MBDiBPDT)_2Cl_2}$; II, $\mathrm{Pd(EBDiBPDT)Cl_2}$; III, $\mathrm{Pd(TrMBDiBPDT)Cl_2}$; IV, $\mathrm{Pd(TtMBDiBPDT)Cl_2}$; V, $\mathrm{Pd(TIBPS)_2Cl_2}$; VI, $\mathrm{Pd(DHS)_2Cl_2}$.

diisobutyl phosphorodithioate groups forces one end of the ligand away from the coordination plane of the Pd(II) ion. From the curves in Fig. 1, it is quite clear that the bidentate bis-ligands provide much more quantitative extraction of palladium than any of the monodentate reagents, under similar extraction conditions.

Pd(II) Loading Capacity of the Ligands under Study. The metal loading capacity of the reagent is an important criteria of a particular solvent extraction system, when its industrial application is concerned.[18] This was evaluated for these ligands by comparing the per cent extraction of Pd(II) following extraction from 1.0 M HCl where the metal and ligand concentrations were selected to match the stoichiometric ratio found in their complexes. The results as given in Table 3, indicate that the TrMBDiBPDT, TtMBDiBPDT, and TIBPS can use more than 90% of the active component in a single extraction, while about 35 and 25% of the ligand remained unused in the cases of extraction with MBDiBPDT and DHS, respectively, even after shaking for 18 h. The alkane-1, ω-diyl bis(O,O-diisobutyl phosphorodithioate)s with a 3 or 4 carbon separation between the two sulfide sulfur atoms are characterized with the highest efficiencies of palladium loading.

Back-Extraction of Palladium(II). To test the feasibility of developing a palladium recovery process based on the ADBDiBPDT reagents, the back-extraction properties of the concerned Pd(II) complexes in DCE were studied using thiourea as the stripping reagent. The back-extraction data (Fig. 4), in general, indicate that Pd(II) can be stripped by acidic thiourea solution from the organic phase containing the complexes of the ligands under consideration. However, as far as the kinetics of back-extraction is concerned, the Pd(TtMBDiBPDT)Cl_2 complex appears to be the best system for the recovery of palladium, providing almost quantitative stripping in about 1 min. TIBPS and TrMBDiBPDT also allow quantitative stripping of palladium but take 3 min to equal the recovery obtained with TtMBDiBPDT. The reagents MBDiBPDT, EBDiBPDT, and DHS have much slower kinetics of back-extraction. It can be noticed that the order of palladium stripping among the monodentate ligands is the one expected from Fig. 1, i.e. the higher the equilibrium $\log D$ values for a given ligand, the less is the ease of back-extraction, but among the bidentate ligands, this order is reversed. This may be attributed to the flexibility or the rigidity of the ligand cavity engaged in the respective complexes. Here, stripping of palladium involves the replacement of the bidentate ligand by thiourea in which a greater flexibility of the ligand cavity in the original complex probably facilitates the rate of substitution. On the basis of the extraction and back-extraction properties of the reagents tested in this work, the TtMBDiBPDT seems to be highly promising for its use in the recovery of palladium from chloride leach sources.

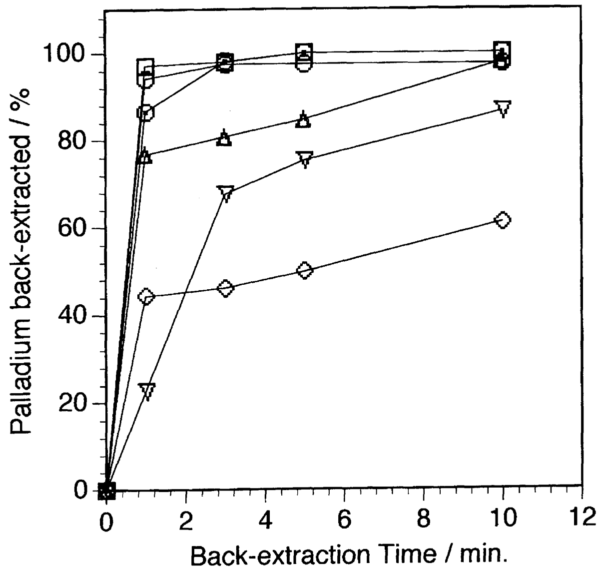


Fig. 4. Back-extraction of palladium from the organic phase. Stripping reagent=5 w/v% thiourea in 0.5 M HCl; $[Pd^{2+}]_{org}=5\times10^{-4}$ M in the from of the extracted complex in DCE. Curves: ◇, Pd(MBDiBPDT)$_2$Cl$_2$; △, Pd(EBDiBPDT)Cl$_2$; ○, Pd(TrMBDiBPDT)Cl$_2$;□, Pd-(TtMBDiBPDT)Cl$_2$;⊙, Pd(TIBPS)$_2$Cl$_2$; ▽, Pd(DHS)$_2$Cl$_2$.

Extraction Constants and Extraction Kinetics. Table 4 lists the extraction constant and the half-life extraction time values of the mono- and bidentate sulfur reagents. The conditional extraction constants ($\log K'_{ex}$) for the extraction of Pd(II) using these ligands show that the stability of Pd(II) complexes of the monodentate sulfur ligands increases in the order: TIBPS < DHS < MBDiBPDT. This means that the sulfur donor in the bis-structure (P–S–C) is more efficient to coordination with Pd(II) than those in DHS (C–S–C) or TIBPS (P=S). In the bidentate series of ligands, the $\log K'_{ex}$

Table 3. Metal Loading Data for the Extraction of Pd(II) with the Selected Reagents

Ligand	Pd(II)/Ligand ratio	%Loading
MBDiBPDT	1 : 2	66.5
EBDiBPDT	1 : 1	88.5
TrMBDiBPDT	1 : 1	99.0
TtMBDiBPDT	1 : 1	95.1
TIBPS	1 : 2	90.6
DHS	1 : 2	74.2

$[Pd^{2+}]=1\times10^{-3}$ M in 1.0 M HCl; [Ligand]=1.0 or 2.0×10^{-3} M in DCE; Shaking Time=18 h; Phase Ratio=1.

Table 4. Extraction Constant (K'_{ex}) and Half-Life Extraction Time ($t_{1/2}$) Values Obtained for Extraction of Pd(II) Using Various Sulfur Reagents

Ligand	K'_{ex}	$t_{1/2}$/h
MBDiBPDT	6.30±0.56	ND[a)]
EBDiBPDT	3.96±0.45	ND
TrMBDiBPDT	4.11±0.26	ND
TtMBDiBPDT	4.62±0.64	3.7
TIBPS	5.33±0.49	7.5
DHS	5.55±0.65	9.2

a) ND means not determined.

value increases in the order of increasing distance between the two donor atoms, signifying that TtMBDiBPDT would be the best reagent for palladium recovery among the bis-coordinated ligands.

The half-life extraction time ($t_{1/2}$) for Pd(II) extraction with TtMBDiBPDT is much shorter than those of TIBPS and DHS as measured under identical conditions of [ligand]= 1×10^{-3} M and [chloride]=1.0 M. The difference in the rate of extraction may arise from the mechanism of extraction in the two coordination types. The interaction of $PdCl_4^{2-}$ with monodentate TIBPS and DHS is known to proceed through a two-step reaction.[16] The bis-coordinated TtMBDiBPDT, on the other hand, is expected to extract Pd(II) in a single step with a shorter $t_{1/2}$ value.

Conclusions

The extraction of Pd(II) was studied using a new series of bifunctional sulfur reagents, ADBDiBPDT. The new compounds as accessible by simple synthesis have better extraction properties than monofunctional TIBPS or DHS. The extraction of Pd(II) from chloride medium using ADBDiBPDTs is characterized with the formation of a 1 : 2 or 1 : 1 metal-ligand complex, depending on the size of the ADBDiBPDT molecule. A solvent extraction procedure based on TtMBDiBPDT may be useful for the selective recovery of palladium from chloride leach sources, where acidic thiourea could be used as the strip phase.

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