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Extraction Behavior of Silver Ion with Open-Chain *S,S′-α,ω*-Alkanediyl *O,O′*-Bis[2-(ethylthio)ethyl]dithiocarbonates

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The *S,S′-α,ω*-alkanediyl *O,O′*-bis[2-(ethylthio)ethyl]dithiocarbonates, which are easily accessible by synthesis, have been used in solvent extraction studies of precious metal ions. Taking *S,S′*-1,3-propanediyl *O,O′*-bis[2-(ethylthio)ethyl]-dithiocarbonate (PbETEdTC) as the representative of this group, the compound appears to have promising efficiency for the extraction of silver from perchlorate media, where the silver ion forms a 1 : 1 extractable complex with PbETEdTC. A quantitative back-extraction process from the organic phase is possible with 5 M HCl. From extraction studies, PbETEdTC proved to be a good extractant for silver in a perchlorate medium. The important role played by structural modifications of the bis(dithiocarbonate) molecule is evidenced by the differences in the silver extractabilities and silver-ligand stoichiometries.

The development of chelating reagents for metal extraction has attracted much interest in recent years. Various ligands have been designed for the selective recovery of metal ions using solvent extraction, liquid membrane extraction and adsorption on chelating resins.[1] Although extraction based on ligands with O- or N-donor atoms is widely known, relatively few studies have been reported on extractants possessing sulfur or phosphorus, as electrically neutral donor atoms.[2] Neutral sulfur-containing ligands, such as thioethers and cyclic polythioethers, have been identified as powerful extractants for silver and other metal ions belonging to the soft acid class.[3] Open-chain thioethers were found to have a higher silver distribution ratio than their cyclic analogues,[4—8] because the silver coordination is better in open-chain compounds having a more flexible structure than the cyclic ones. Alkyl dithiocarbonates, commonly known as xanthates, containing one thione and thiole sulfur, also act as strong ligands to many metal cations.[9] Although these rather inexpensive compounds have been used extensively in metal floatation and to some extent in analytical chemistry,[9] their use in the solvent extraction of metal ions has not been well established. This is because of the fact that simple alkyl dithiocarbonates are considerably water soluble. Conversely, their metal complexes are rather insoluble in common organic solvents. Their coordination with metal cations is very wide and unselective. In order to utilize the alkyl dithiocarbonic acid derivatives in solvent extraction, our aim was to synthesize acyclic neutral bis(molecules) having better complexation selectivity and higher ligand lipophilicities. Furthermore, the bis(molecules) are expected to behave in similar manner in which the sulfur atoms of the acyclic compounds are able to provide preferable circumstances to associate with Ag^+ compared to those of the cyclic ones. In this regard, we have already reported the extraction of Pd(II) and Ag(I) using bis-derivatives of butyldithiocarbonic acids[10,11] In the present paper we wish to report on the extraction of silver with a new class of acyclic neutral sulfur ligands, namely the *S,S′-α,ω*-alkanediyl *O,O′*-bis[2-(ethylthio)ethyl]dithiocarbonates. The presence of six sulfur donors in an open-chain structure of considerable flexibility is expected to provide interesting coordination and extraction properties towards the Ag(I) cation.[4,12—15] Moreover, the variation in the spatial distances among the donating sulfur atoms would further give insight into the extraction selectivity of the neutral sulfur ligands as a whole.

The synthesis of *S,S′-α,ω*-alkanediyl *O,O′*-bis[2-(ethylthio)ethyl]dithiocarbonate is described, taking *S,S′*-1,3-propanediyl *O,O′*- bis[2- (ethylthio)ethyl]dithiocarbonate (PbETEdTC) as the representative of this new group. The extraction behavior for some transition metal ions, the effect of an anion on silver-extractant complexation and the silver extractabilities with PbETEdTC together with a analogous compound, *S,S′*-1,3-propanediyl *O,O′*-dibutyldithiocarbonate (PdBdTC), are discussed.

Experimental

Reagents. Ligands PbETEdTC, *S,S′*-1,4-butanediyl *O,O′*-bis-[2-(ethylthio)ethyl]dithiocarbonate (BbETEdTC) and *S,S′*-1,3-propanediyl *O,O′*-di-*s*-butyl dithiocarbonate (PdsBdTC) were prepared by similar methods as those described in a previous paper,[10] except that a 2-(ethylthio)ethanol ($CH_3CH_2SCH_2CH_2OH$) for PbETEdTC and BbETEdTC and *s*-butyl alcohol for PdsBdTC were used as one of the starting materials. The products were purified, and identification of the products was carried out using ^{1}H NMR and FTIR spectroscopies and elemental analysis. The results of the analyses and some physical properties are as follows:

PbETEdTC: Yellowish liquid; bp > 100 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.29$ (t, 6H, CH_3–), 2.14 (q, 4H, –CH_2–), 2.67 (q, 4H, –CH_2–), 2.83 (q, 4H, –CH_2–), 3.17 (m, 4H, –CH_2–), 4.75 (t, 4H, –CH_2–).

Found: C, 41.67; H, 6.51%. Calcd for $C_{13}H_{24}O_2S_6$: C, 41.63; H, 6.52%.

BbETEdTC: Light green liquid, bp > 100 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.29$ (t, 6H, $-CH_3$), 1.83 (m, 4H, $-CH_2-$), 2.74 (q, 4H, $-CH_2-$), 2.90 (t, 4H, $-CH_2-$), 3.17 (m, 4H, $-CH_2-$), 4.75 (t, 4H, $-CH_2-$). Found: C, 40.11; H, 6.26%. Calcd for $C_{14}H_{26}O_2S_6$: C, 40.16; H, 6.26%.

PdsBdTC: Yellowish liquid; bp > 200 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.28$ (t, J=8.0 Hz, 6H, $-CH_3$), 1.54 (d, J=6.8 Hz, 6H, $\rangle C-CH_3$), 1.83 (m, 4H, Me–CH_2-), 2.7 (m, J=8.1 Hz, 2H, $-S-C-CH_2-C-S-$), 3.17 (t, J = 9.1 Hz, 4H, $-S-CH_2-$), 5.61 (m, J = 7.8 Hz, 2H, $\rangle CH-O-$). FTIR 1063 (ν C=S); 1221 (ν C–O); 741 cm^{-1} (ν C–S). Found: C, 47.42; H, 7.39%. Calcd for $C_{13}H_{24}O_2S_4$: C, 47.41; H, 7.39%.

The preparations and properties of *S,S'*-1,3-propanediyl *O,O'*-dibutyl dithiocarbonate (PdBdTC), *S,S'*-1,4-butanediyl *O,O'*-dibutyl dithiocarbonate (BdBdTC), *S,S'*-1,3-propanediyl *O,O'*-diisobutyl dithiocarbonate (PdiBdTC), and *S,S'*-1,4-butanediyl *O,O'*-diisobutyl dithiocarbonate (BdiBdTC) were reported in a preceeding paper.[10)]

A silver stock solution (1 mg mL^{-1}) was prepared by dissolving 1.5748 g $AgNO_3$ in water and diluting to 1 liter. Other metal ion solutions were prepared by dissolving their nitrate or chloride salts in water. The diluent, 1,2-dichloroethane (DCE), was saturated with water before use so as to prevent any volume changes of the phases during extraction. All of the reagents used were of analytical grade. Distilled and deionized water was used throughout the experiments.

Procedures. An aqueous solution (10 mL) containing the metal salt and any other of the required reagents was shaken at a speed of 300 oscillations/min with a solution (10 mL) of the extractant in DCE in a 50-mL glass stoppered cylindrical tube at 25 °C for a predetermined time. After phase separation, the metal concentrations in the aqueous phase were measured by AAS using the Daini Seikosha AAS Model SAS/727; the metal concentrations in the organic phase were calculated by the mass balance of the metal content in the aqueous phase both before and after equilibration.

Back-extraction experiments were performed as follows: An aliquot (10 mL) from the separated organic solution was shaken with an aqueous stripping solution (10 mL) at 25 °C, and the metal ion in the aqueous solution was measured.

The distribution of PbETEdTC between the organic and aqueous phases was determined by a gravimetric method.[16)] Equal volumes (25 mL) of 4.8×10^{-2} M (1 M = 1 mol dm^{-3}) PbETEdTC in DCE and deionized water were brought to equilibrium at 25 °C under the conditions used in the extraction experiments. After phase separation, the DCE phase was evaporated, dried in vacuo (< 0.5 Torr, 1 Torr = 133.322 Pa) for 24 h, and then weighed. The aqueous phase was extracted with DCE (25 mL×3), and the combined extracts were evaporated, dried in vacuo and weighed.

Results and Discussion

The partition coefficient (C_{org}/C_{aq}) of PbETEdTC between dichloroethane and water was determined and evaluated to be 3.0×10^2, suggesting that these compounds of *S,S'*-α,ω-alkanediyl *O,O'*-bis[2-(ethylthio)ethyl]dithiocarbonate structure are favorable as solvent extraction reagents.[17)] Unlike alkali and alkaline-earth metal dithiocarbonates,[9,18)] bis(dithiocarbonates) are found to be stable at ambient temperature, pressure, in air and in the presence of mineral acids up to at least 3 M of the acid concentration, and showed no changes in their spectral properties, even after several months of storage.

For an extended shaking time of up to 10 h, an effective separation of the two phases and the silver extractability were maintained, as shown in Fig. 1. Although the extraction of Ag^+ with PbETEdTC appeared to reach equilibration in 1 h, in the later part of the experiment, an 8 h contact time was used to ensure complete equilibration.

The extractabilities of silver with *S,S'*-α,ω-alkanediyl *O,O'*-bis[2-(ethylthio)ethyl]dithiocarbonates, together with other *S,S'*-α,ω-alkanediyl *O,O'*-dibutyl dithiocarbonates, are tabulated in Table 1. The extractability is highly dependent on the length of the carbon chain joining the two *O*-alkyl dithiocarbonate groups, as shown between ligands 1–2, 4–5, and 6–7. The extractability of the ligands containing a $-(CH_2)_3-$ chain was better than those containing a $-(CH_2)_4-$ chain, because it is capable of forming a stable 6- or 7-membered chelate ring[19)] with the optimum Ag^+–S distance. The extractability is also dependent on the alkyl group attached to the dithiocarbonate, as illustrated in ligands 1, 3, 4, and 6, and decrease in the following order: 2-(ethylthio)ethyl > butyl > isobutyl > *s*-butyl. This is because of steric factors towards the donor sites of the molecules and the greater electron-releasing tendency of the diethylthionyl group. For PbETEdTC and BbETEdTC, this seems that enhanced Ag^+ extraction arises from coordination with the sulfur atoms in the 2-(ethylthio)ethyl groups.

Based on the observed extractabilities given in Table 1, the *S,S'*-α,ω-alkanediyl *O,O'*-bis[2-(ethylthio)ethyl]dithiocarbonates are generally better extractants for Ag^+ than the *S,S'*-α,ω-alkanediyl *O,O'*-dibutyl dithiocarbonate derivatives, and should be efficiently used as extractants for Ag^+. The extraction behavior of Ag^+ has been studied in detail, with special attention being paid to PbETEdTC and BbETEdTC as the representative of the bis(dithiocarbonate) compounds, and together with an analogous compound, PdBdTC.

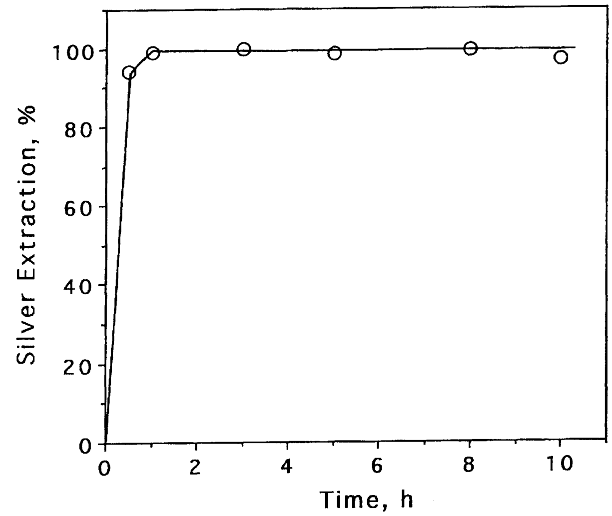
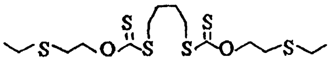
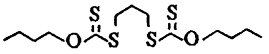
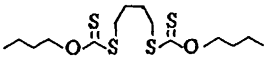
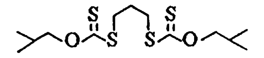
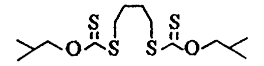


Fig. 1. Effect of shaking time on the equilibration of silver extraction with PbETEdTC. [PbETEdTC] = 2.5×10^{-3} M in DCE, [Ag^+] = 1.0×10^{-4} M in 0.1 M $NaClO_4$, phase ratio = 1.

Table 1. Extraction of Silver with Different *S,S'*-α,ω-Alkanediyl *O,O'*-Dialkyldithiocarbonates

		Ligands	Extraction/%	RSD/%
1	PbETEdTC		99.2	0.1
2	BbETEdTC		98.2	0.2
3	PdsBdTC		22.2	0.6
4	PdBdTC		96.1	1.1
5	BdBdTC		93.2	1.3
6	PdiBdTC		56.8	5.4
7	BdiBdTC		17.2	2.0

[Ligand] = 2.5×10^{-3} M in DCE, [Ag$^+$] = 1.0×10^{-4} M in 0.1 M NaClO$_4$, phase ratio = 1, shaking time = 1 h.

To evaluate the nature of the Ag$^+$ coordination, the Ag$^+$-ligand stoichiometries were determined for PbETEdTC and BbETEdTC in a perchlorate medium. In the slope ratio method, log *D* vs. log [L] plots of PbETEdTC and BbETEdTC, where *D* is the distribution ratio of Ag$^+$ between the organic and aqueous phases and [L] is the ligand concentration (Fig. 2), yielded straight lines with a slope of approximately 1. The results given in Fig. 2 definetely prove that from a 0.1 M NaClO$_4$ solution these ligands extract Ag$^+$ through the formation of 1 : 1 silver-ligand complexes. However, log *D* vs. log [L] plots of PdBdTC and PdiBdTC gave slope values of 2, proving that these ligands extract Ag$^+$ through the formation of 1 : 2 silver-ligand complexes (also shown in Fig. 2). Since the coordinating abilities of the various types of sulfur donors decrease in the order RS$^-$ > R$_2$S > RC=S$\gg$ring sulfur,[20] it can be assumed that the extraction of Ag$^+$ occurs preferentially through coordination by the thioether sulfur atoms in the bis-molecule. The formation of a 1 : 1 Ag : PbETEdTC or 1 : 1 Ag : BbETEdTC complexes is indicative that the sulfur atoms of the attached alkyl chain in the bis(dithiocarbonate) molecule takes part in the coordination.

The preferred coordination number of Ag$^+$ is two and with a linear geometry.[21] Some dithioethers are known to form chelate rings and tetrahedral coordination around the silver ion.[4,6,22] Tetrahedral complexes of Ag$^+$ with sulfur donor ligands, such as [Ag(SCN)$_4$]$^{3-}$ and [AgSCN(PPr$_3$)$_3$], also exhibit good stability.[12] From the observed stoichiometry of the Ag$^+$ extraction using the presented ligands, it is certain that each Ag$^+$ ion is coordinated to four sulfur atoms. This idea is based on the fact that the present ligands contain at least two thioether donors at exactly equivalent positions. Thus, the stability requirements would lead to a four-coordinate tetrahedral geometry for the extracted complex on the basis of the stabilization of 6- and 7-membered S–Ag–S rings in the coordination sphere. In other words, the spatial distribution of the donors and the flexibility of the ligand structure enforces a rearrangement in the relatively strain-free tetrahedral configuration. This assumption probably resembles the situation of tetrahedral silver coordination with acyclic tetrathioethers.[4,7,22,23]

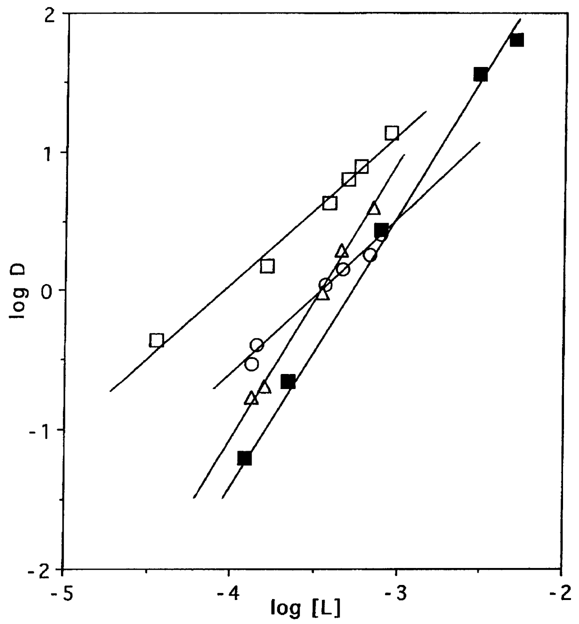


Fig. 2. Determination of the stoichiometry of the Ag$^+$–ligand complexes using the slope ratio method. Ligand and slope value: (□) PbETEdTC = 0.96, (○) BbETEdTC = 1.07, (△) PdBdTC = 2.00, (■) PdiBdTC = 1.96. Extraction Parameters: [ligand] = 1.0×10^{-4} to 5×10^{-3} M in DCE, [Ag$^+$] = 1.0×10^{-4} M in 0.1 M NaClO$_4$, shaking time = 8 h, phase ratio = 1.

The influence of counter ions on the extraction of silver with PbETEdTC was studied by incorporating increased amounts of ClO$_4^-$, Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ ions separately in the aqueous phase while keeping the ligand concentration constant. The concentrations of the anions ranged from 0.1—5.0 M, by adding the corresponding acids instead of their neutral salts in order to ensure homogenuity in both phases. For a comparison, the effects of adding $NaClO_4$ and aqueous NH_3 were also studied in a similar way. The results are shown in Fig. 3. The variation of the H^+ ion in the aqueous phase has little or no effect on the extractability of Ag^+ with the present ligand, as is evident from the extraction curves for $NaClO_4$ and $HClO_4$ in Fig. 3. Both $NaClO_4$ and $HClO_4$ provide similar extractabilities at low concentrations. With an increase of $NaClO_4$ in the aqueous phase, the extraction of Ag^+ falls off due to a "salting-in" effect,[24] whereas the extraction remains to be unaffected in the $HClO_4$ system. In fact, the two curves should coincide if the reversibility of extraction were maintained in both cases. The extraction of Pd^{2+} with other neutral sulfur ligand was also found to be independent of the aqueous acid concentration.[10]

Considering the effects of counter anions, it is seen that the extraction of silver is quantitative at all concentrations of $HClO_4$. This is quite expected, because perchlorate does not form stable aqueous complexes with the Ag^+ cation. Moreover, the high lipophilicity of the perchlorate ion permits an easy formation of Ag–PbETEdTC–ClO_4 complexes in the organic phase. In a chloride medium, Ag is not extracted at all, with obvious precipitation of AgCl at low (< 1.0 M) HCl concentrations. At higher aqueous HCl concentrations, silver exists predominantly as anionic chlorocomplexes viz. $AgCl_4^{3-}$, $AgCl_3^{2-}$. These complexes are known to be highly stable and, thus, to prevent the interaction of Ag^+ with the ligand. This phenomenon was also observed in the extraction of silver with some thioether extractants, indicating that the Ag^+–sulfur complexes are in general less stable than the corresponding aqueous silver-chloro complexes.[25]

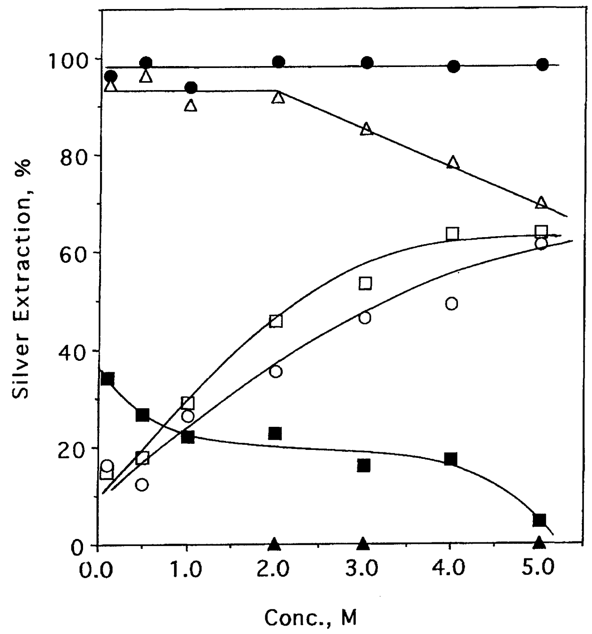


Fig. 3. Determination of silver extractability in different aqueous medium with PbETEdTC. aqueous medium: (△) $NaClO_4$, (○) NH_3, (□) HNO_3, (■) H_2SO_4, (●) $HClO_4$, (▲) HCl. Extraction Parameters: [PbETEdTC] = 2.5×10^{-3} M in DCE, [Ag^+] = 1.0×10^{-4} M, shaking time = 1 hour, phase ratio = 1.

In the ideal case, the extraction of silver by PbETEdTC from sulfate and nitrate media should increase linearly with an increase in the anion concentration in the aqueous phase, since neither SO_4^{2-} nor NO_3^- is known to yield stable complexes with Ag^+ in aqueous acid solutions. However, from the data given in Fig. 3, it appears that the extractability of silver is restricted by the lipophilicities of the concerned anions and by the diluent-solute interactions. In the lipophilicity series of inorganic anions, both NO_3^- and SO_4^{2-} occupy low positions following ClO_4^- and Cl^-, respectively. Thus, the formation of extractable Ag–ligand–nitrate or Ag–ligand–sulfate complexes in the organic phase is firstly hindered by the diminishing lipophilicities of NO_3^- and SO_4^{2-}. Secondly, the solubility of the extracted complex in the organic phase is of great concern, especially with sulfate. In a diluent like DCE ($\varepsilon_r = 10.6$), the solubility of the Ag–ligand–sulfate complex is definitely very low. The experimental curves in Fig. 3 most probably reflect the above factors, particularly at higher SO_4^{2-} concentrations. The decreasing extractabilities of Ag^+ at increasing H_2SO_4 concentrations were also observed with other neutral sulfur-containing extractants.[26] For extraction in a nitrate medium, it may be envisaged that the lipophilicity factor is far more dominant than the solubility factor in determining the overall extractability.

It is very interesting to note that the extraction of Ag increases remarkably with the addition of aqueous NH_3 in the extraction system. This would mean that the silver–ammine complexes formed in the aqueous solution are quite labile towards substitution by sulfur donors in the PbETEdTC molecule. It can also be noticed that the extraction isotherm observed with aqueous NH_3 is almost parallel to that in a nitrate medium. This may be interpreted by the fact that the nitrate ions present in the original $AgNO_3$ solution actually enter the organic phase to act as a counter anion of the Ag–ligand complex. Hence, the extraction is again regulated by the properties of the NO_3^- ion.

Summarizing the observed effects of counter anions on the extraction of Ag with PbETEdTC, the extractability order can be arranged as: $ClO_4^- \gg NO_3^- > SO_4^{2-} > Cl^-$.

The usual way of stripping Ag^+ from the organic phase is through the use of thiourea,[11] which is unstable under the usual conditions, and is expensive. We tried the back-extraction of Ag^+ with 5 M HCl on the basis of the higher stability and solubility of the silver-chloro species in HCl solutions. The results of silver stripping with various reagents are compared in Table 2.

To justify the practical application of this work, the selectivity of silver extraction with PbETEdTC and PdBdTC was tested on a mixed solution containing the common metals in 0.1 M $NaClO_4$. Cobalt, cadmium, copper, chromium, iron, nickel, manganese, lead, palladium, and zinc were selected as the matrix elements. The experimental conditions and the results are summarized in Table 3. Silver was separated quantitatively from the transition metal ions. Pt^{4+}, Au^{+3}, and Sn^{4+} caused precipitation in the extraction system when any of these elements were added into the synthetic solution.

Table 2. Back-Extraction of Silver Ion from the Silver–Ligand Complex with Different Reagents for 1 h Shaking Time and Phase Ratio of 1

Reagents	Ag back-extracted/% (RSD/%)			
	Ag^+–PbETEdTC–ClO_4^-		Ag^+–PdBdTC–ClO_4^-	
5 M HCl	100	(0.01)	100	(0.01)
5 M HNO_3	12.9	(1.1)	8.1	(0.5)
5 M H_2SO_4	21.2	(6.3)	36.7	(0.2)
5 M $HClO_4$	0	(N. a.)[a]	0	(N. a.)[a]
5 M NH_3	17.3	(0.04)	2.0	(2.9)

a) N. a. means not applicable.

Table 3. Extraction of Metals with PbETEdTC and PdBdTC from a Synthetic Mixed-Metal Solution in 0.1 M $NaClO_4$

Element	Extraction/% (RSD/%)	
	PbETEdTC	PdBdTC
Ag^+	84.7 (1.2)	83.4 (0.7)
Pd^{2+}	96.3 (0.01)	95.5 (0.1)

Metal ions not extracted with both ligands: Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Sn^{2+}, Pb^{2+}, Zn^{2+}.

Interfering ions which cause precipitation: Pt^{4+}, Au^{3+}, Sn^{4+}.

[synthetic mixture] = containing 1×10^{-4} M each of the mentioned metal in 0.1 M $NaClO_4$, [Ligand] = 2.5×10^{-3} M in DCE, shaking time = 1 h, phase ratio = 1.

Pd^{2+} was co-extracted with Ag^+, having an antagonistic effect on the extraction of silver. This was expected, because of the considerable affinity of sulfur donors for soft Pd^{2+} ion.[19)]

By means of an HCl back-extraction system, it is possible to develop a procedure for separating silver from palladium, and providing a promising efficiency for the recovery of silver. It is suggested that the palladium chelate with PdBdTC or PbETEdTC is more stable than that of silver chelate with PdBdTC or PbETEdTC, as revealed in Table 3. By the test shown in Table 4, with single stripping using 5 M HCl, silver was back-extracted while palladium remained in the organic phase, even when a large amount of palladium was present in the organic phase. The observed retention of silver in the organic phase in the presence of palladium was most probably due to a slowing down of the silver back-extraction kinetics by the Pd^{2+} complex. The Pd^{2+} complex, presumably possessing a high interfacial reactivity, hinders the transfer of Ag^+ to the aqueous phase, resulting in an incomplete stripping of Ag^+ within the stipulated contact time. In terms of selectivity, good results were obtained for the ligands tested, and PbETEdTC again proved to be a better extractant than PdBdTC. The presented ligands would be highly efficient for the selective extraction of palladium, and the quantitative stripping of residual palladium from the organic phase can be made possible by using 0.5 M acidic thiourea solutions in a cross-current multiple-contact stripping procedure.[10)]

Table 4. Back-Extraction of Silver Ion from the Organic Phase Loaded with Ag^+ and Pd^{2+} Using 5 M HCl as Stripping Agent

Organic phase	Back-extraction/% (RSD/%)	
	Ag^+	Pd^{2+}
Mixture with PbETEdTC	65.9 (5.6)	0 (N. a.)[a]
Mixture with PdBdTC	53.8 (2.9)	0 (N. a.)[a]

Phase ratio = 1, Shaking time = 1 h. a) N. a. means not applicable.

Conclusion

This study points out that *S,S'*-α,ω-propanediyl *O,O'*-bis[2-(ethylthio)ethyl]dithiocarbonate (PbETEdTC), which is easily accessible by synthesis, appears to have a more promising efficiency for the extraction of silver from a perchlorate media than does *S,S'*-1,3-propanediyl *O,O'*-dibutyl dithiocarbonate (PdBdTC). Silver ion formed a 1 : 1 extractable complex with PbETEdTC, while PdBdTC formed a 1 : 2 complex with Ag^+. Transition metals were not extracted, while Au^{3+}, Pt^{4+}, and Sn^{4+} produced troublesome precipitation. The extraction of Ag^+ is quantitative in a perchlorate medium. While in nitrate, sulfate and aqueous ammonia media, it is regulated by the properties of the interfacial species. The back-extraction of Ag^+ can be easily accomplished with 5 M HCl.

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