EXTRACTION OF COMPLEXES OF SOME METALS WITH 1,1-DISUBSTITUTED 3-DIPHENOXYTHIOPHOSPHORYLTHIOUREAS

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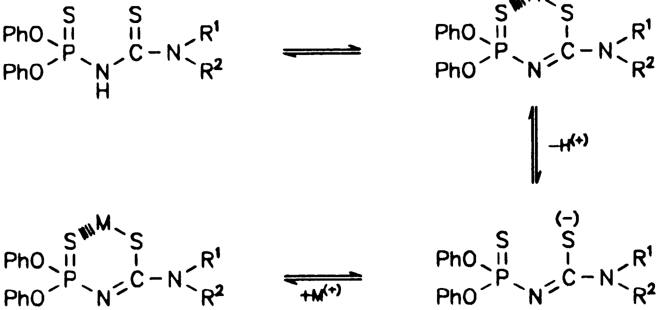
Received February 17, 1992
Accepted May 10, 1992

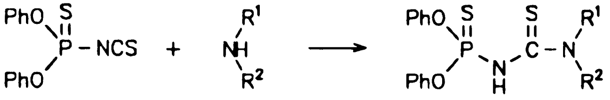
The extraction of complexes of silver, mercury, cadmium, cobalt, zinc, scandium and some rare earth elements (Ln) into benzene solutions of 1,1-disubstituted 3-diphenoxythiophosphorylthioureas (HA) containing alkyl and aryl substituents was examined using the radiotracer technique. The complexes AgA(HA), HgA_2, CdA_2 and LnA_3 are extracted into the organic phase, and the extraction increases in order Co, Zn, Cd ≈ Ln << Hg < Ag. The extraction constants were calculated. During the extraction process using medium acidic aqueous phases (1 M HNO_3), the reagents decompose into the corresponding amines and $(PhO)_2P(S)NCS$.

1,1-Disubstituted 3-diphenoxythiophosphorylthioureas, $(PhO)_2P(S)NHC(S)NR^1R^2$ (HA), where R^1 and R^2 are alkyl and/or aryl groups, are weak acids ($pK \approx 7 - 9$) which are well soluble in benzene, toluene and chloroform[1 – 3] and form extractable chelates according to the general Scheme 1



SCHEME 1

(the resonance structures are not shown for simplicity). Their synthesis proceeds by the substitution or addition mechanism. Addition from dry ether can be written as



SCHEME 2

The two components react readily in the molar ratio 1 : 1; the reaction is quantitative except for diphenylamine[2]. If, in solvent extraction, a mineral acid is present in the aqueous phase at a concentration not lower than 1 mol l^{-1}, the reaction is reversible and $[H_2NR^1R^2]^+$ cations are formed and pass into the aqueous phase. The formation of chelate complexes according to Scheme 1 is thereby suppressed[2,3].

In the present work, the extraction of selected metals from aqueous hydrochloric or nitric acid with 1,1-disubstituted 3-diphenoxythiophosphorylthioureas was studied. The metal distribution between the two liquid phases was measured radiometrically using the tracer technique.

EXPERIMENTAL

Chemicals and Apparatus

The 1,1-disubstituted 3-diphenoxythiophosphorylthioureas were synthesized according to Scheme 2 by stirring equimolar quantities of $(PhO)_2P(S)NCS$ and HNR^1R^2 in dry ethyl ether for 5 min. Thereafter the liquid phase was gently evaporated under an infrared lamp and the residue was taken up in dry benzene. The purity of the products was checked by ^{31}P NMR spectrometry. The reagents themselves gave a single signal at $\delta(^{31}P)$ 52 – 54 ppm, while the initial $(PhO)_2P(S)NCS$ (henceforth *I*) exhibited $\delta(^{31}P)$ 35.4 ppm (ref.[2]). The latter was synthesized following the procedure by Levchenko and Zhmurova[4]. In the derivatives prepared, R^1 and R^2 were $(propyl)_2$ (*II*), $(butyl)_2$ (*III*), $(isobutyl)_2$ (*IV*), H, tert-butyl (*V*), H, heptyl (*VI*), $(octyl)_2$ (*VII*), H, *p*-tolyl (*VIII*), $(cyclohexyl)_2$ (*IX*), and methyl, phenyl (*X*). To assess the necessity for the reagent to contain sulfur in the $-NHC(S)NR^1R^2$ group, the compound $(PhO)_2P(S)NHC(O)N$-(methyl, phenyl) (*X**) was also synthesized as an analogue of reagent *X*. The synthesis pathway was as with the sulfur analogue, and its purity was also checked by ^{31}P NMR spectrometry[2] ($\delta(^{31}P)$ 53.7 ppm).

The other chemicals used were of reagent grade purity.

The radiotracers ^{46}Sc, ^{60}Co, ^{65}Zn, ^{109}Cd, ^{110m}Ag, $^{152+154}Eu$, ^{170}Tm and ^{203}Hg were commercial products (CIS, Poland). They were used in the form of solutions in HCl (0.1 mol l^{-1} for Co and Zn, 0.5 mol l^{-1} for Hg), $HClO_4$ (0.1 mol l^{-1} for Sc, Cd, Eu, Tm) and HNO_3 (0.1 and 1.0 mol l^{-1} for Ag). Their specific activities (10^3 Bq cm^{-3}) and concentrations (μmol l^{-1}) in the working solutions were as follows: Sc 10 – 30, 1; Co 3.5, 44; Zn 2, 2; Ag 1, 0.3; Cd 30, 80; Eu 2.5, 0.06 – 0.1; Tm 3, 14; Hg 20, 0.6 – 5.

The gamma radioactivity was measured on an 1185 Automatic Gamma Counting System (Nuclear Chicago, U.S.A.), the ^{31}P NMR spectra were scanned on Bruker WP-200 and Bruker AC-80 instruments.

Procedure

The working solutions of the reagents in benzene were prepared always fresh to be processed the same day. Five ml of each of the organic and aqueous phase were agitated on a rotary shaking machine for

5 min (for mineral acid concentrations 0.5 and 1.0 mol l^{-1}) or 10 min (for mineral acid concentration 0.1 mol l^{-1}) at 20 ± 1 °C, unless stated otherwise.

After phase separation, 2 ml aliquots of each phase were taken and their gamma radioactivity was measured in glass vials. The relative standard deviation of the measurements did not exceed 2%.

RESULTS AND DISCUSSION

Metal Distribution and Extraction Kinetics

The extractability of the metals was investigated via their extraction from an aqueous solution containing a mineral acid (0.1 mol l^{-1}; for Hg, 0.5 ml l^{-1}) into benzene solutions of reagents *IV* and *X*. The results are given in Table I as the log *c* values (*c* is the analytical concentration of the reagent) for which the metal distribution ratio is equal to one. The data demonstrate that only silver and mercury are extracted into the organic phase to a substantial extent, the remaining metals require high starting concentrations of the reagents (at least 1 . 10^{-2} mol l^{-1}). Therefore, the two former metals were employed for the further study.

The extraction kinetics was investigated with silver. If the acidity of the aqueous phase is not very high (0.1 mol l^{-1}), silver passes into benzene solutions of the reagents *I* through *X* so that no later than in 10 min of extraction, the distribution ratios attain constant values; the distribution ratio then does not change even if the extraction is extended to 1 h, which indicates that the organic phase is stable. The distribution of silver between HNO_3 (1 mol l^{-1}) and benzene solutions of the reagents (*II*, *III*, *IV*, *VI*, *VII*: 2 . 10^{-6} mol l^{-1}; *VIII*: 3 . 10^{-6} mol l^{-1}; *IX*: 2 . 10^{-5} mol l^{-1}; *I*: 5 . 10^{-5} mol l^{-1}) was also examined. Figure 1 demonstrates that the extraction equilibrium only establishes with reagents *I* and *VI*, whereas with the remaining reagents the silver distribution ratio

TABLE I
Extractability of metals from mineral acids (0.1 mol l^{-1}) with reagents *IV* and *X* in benzene, expressed as the reagent concentration for 50% extraction efficiency

Metal	Acid	$-\log c_{IV}$	$-\log c_X$
Ag	HNO_3	7.2	7.0
Hg	HCl^a	5.1	5.4
Tm	$HClO_4$	1.7	1.8
Sc	$HClO_4$	1.7	1.5
Cd	$HClO_4$	–	1.4
Eu	$HClO_4$	1.6	1.2
Co	HCl	1.2	0.9
Zn	HCl	1.1	0.6

[a] c_{HCl} = 0.5 mol l^{-1}.

reaches its maximum in 5 to 10 min, thereafter it decreases with stirring time, the decrease accelerating in order *VIII* < *IV* < *III* < *II* < *VII* < *IX*. This indicates that the decomposition of the reagents in acid solutions at $c(H^+) \geq 1$ mol l^{-1} is least marked for R^1 = H and slows further down with increasing length of the aliphatic chain in R^1, R^2. It is fast for reagent *IX* where $R^1 = R^2$ = cyclohexyl. Therefore, a time of extraction of 5 min was chosen for the subsequent measurements of distribution of silver from 1 M HNO_3.

Distribution of Silver

The distribution of silver between aqueous HNO_3 (1 mol l^{-1}) and benzene solutions of reagents *I* through *X* in dependence on their starting concentration is shown in Fig. 2. The high concentration of nitric acid was chosen because the transition of silver complexes into the organic phase is substantial and an excess of reagent against silver ions must be maintained.

Figure 2*a* demonstrates that reagent *I*, containing the functional group P(S)NCS only, forms a well-extractable silver complex whose transfer into the organic phase requires a relatively high starting concentration, $c_I \geq 5 \cdot 10^{-4}$ mol l^{-1}. For the other reagents, their extracting ability with respect to silver decreases in order *VII* > *IV* > *II* > *III* > *X* > *V* > *VI* > *VIII* > *IX*; this series indicates that alkyls are more favourable substituents than aryls and their optimum length is about C_4 to C_8. The slopes of the left segments of the extraction curves of reagents *II* through *X* (Fig. 2) attain a maximum of 2.0 ± 0.3.

The dependence of the silver distribution on the acidity of the aqueous phase at a constant concentration of selected reagents is shown in Fig. 3. The slopes attain a minimum value of −1. Thus, the extraction of silver with the reagents *II* through *X* apparently obeys the pathway

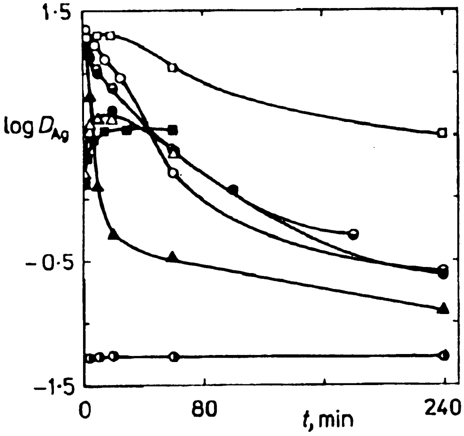


FIG. 1

Dependence of silver distribution ratio on time: $c(HNO_3) = 1$ mol l^{-1}, $c(Ag) = 2.56 \cdot 10^{-7}$ mol l^{-1}, $c(HA)$ (mol l^{-1}): $2 \cdot 10^{-6}$ ● *II*, ⊖ *III*, □ *IV*, ■ *VI*, ○ *VII*; $3 \cdot 10^{-6}$ △ *VIII*; $2 \cdot 10^{-5}$ ▲ *IX*, $5 \cdot 10^{-5}$ ◑ *I*

$$\mathrm{Ag}^+ + 2\,(\mathrm{HA})_{\mathrm{org}} \rightleftharpoons [\mathrm{AgA(HA)}]_{\mathrm{org}} + \mathrm{H}^+ \qquad (A)$$

with the extraction constant

$$K_{\mathrm{ex}} = \frac{[\mathrm{AgA(HA)}]_{\mathrm{org}}\,[\mathrm{H}^+]}{[\mathrm{Ag}^+]\,[\mathrm{HA}]^2_{\mathrm{org}}} = D_{\mathrm{Ag}}\,\frac{[\mathrm{H}^+]}{[\mathrm{HA}]^2_{\mathrm{org}}}\,, \qquad (1)$$

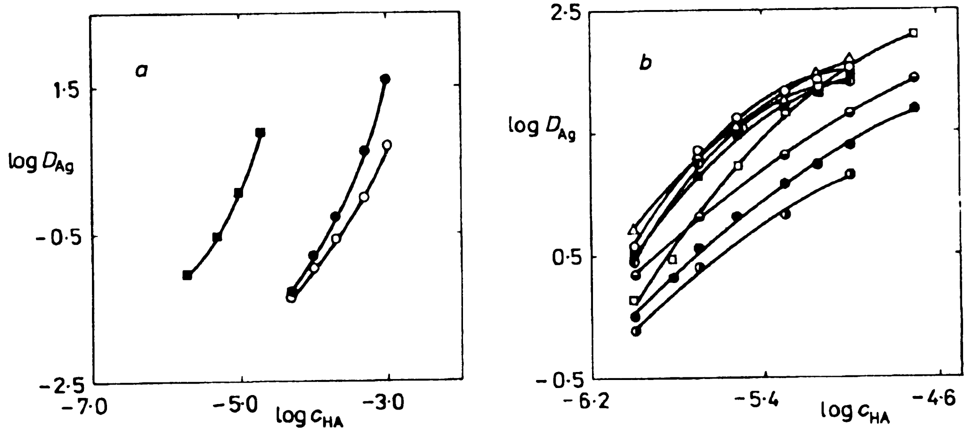


FIG. 2

Distribution of silver in dependence on the starting reagent concentration in benzene. $c(\mathrm{Ag}) = 2.56 \cdot 10^{-7}$ mol l^{-1}, $c(\mathrm{HNO_3}) = 1$ mol l^{-1}. *a* ● *I*, ■ *IX*, ○ *X**; *b* ■ *II*, ◐ *III*, ○ *IV*, □ *V*, ● *VI*, Δ *VII*, ◑ *VIII*, ◒ *X*

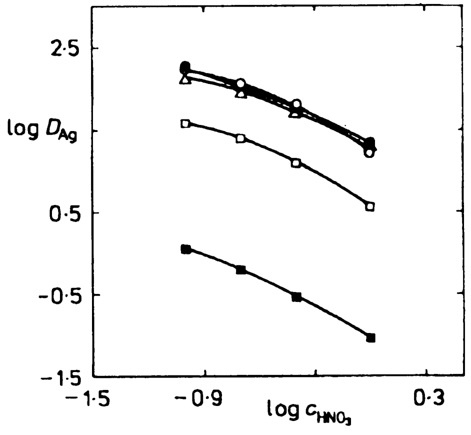


FIG. 3

Distribution of silver in dependence on the starting nitric acid concentration in the aqueous phase. $c(\mathrm{Ag}) = 2.56 \cdot 10^{-7}$ mol l^{-1}, $c(\mathrm{HA}) = 2 \cdot 10^{-6}$ mol l^{-1}. ○ *III*, ● *IV*, □ *VI*, Δ *VII*, ■ *IX* where D_{Ag} is the silver distribution ratio. The values of the extraction constant are given in Table II.

With the oxygen analogue of reagent *X* (i.e. reagent *X**), the extractability of silver was appreciably lower (Fig. 2*a*). Hence, the presence of sulfur in the $-NHC(S)NR^1R^2$ group seems to be prerequisite for the formation of the best-extractable silver complex.

Distribution of Mercury

Figure 4 shows the distribution of mercury between HCl (0.5 mol l^{-1}) and benzene solutions of reagents *I*, *III*, *VIII*, *IX* and *X* in dependence on their concentrations. The oxygen analogue *X** was also used.

The slopes of the curves attain a maximum value of 2.0 ± 0.2. The starting concentration of HCl was chosen higher for mercury than for silver with regard to the

TABLE II
Extraction constants of silver and mercury[a]

Reagent	$(\log K_{ex})_{Ag}$	$(\log K_{ex})_{Hg}$	Reagent	$(\log K_{ex})_{Ag}$	$(\log K_{ex})_{Hg}$
I	7.1	17.5	*VI*	12.0	–
II	12.4	–	*VII*	12.5	–
III	12.4	25.8	*VIII*	11.9	22.0
IV	12.4	–	*IX*	10.1	22.2
V	12.1	–	*X*	12.4	22.4
			*X**	6.6	17.5

Composition: [a] AgA(HA); [b] HgA_2.

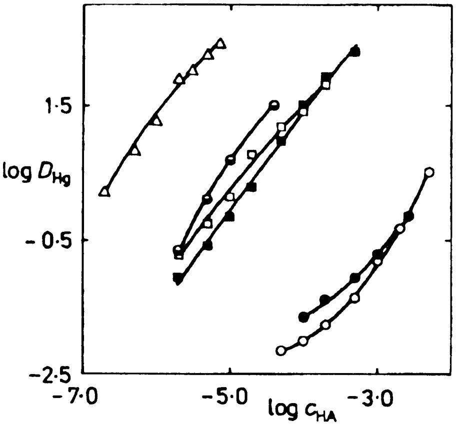


FIG. 4
Distribution of mercury in dependence on the starting reagent concentration in benzene. c(Hg) = 1.87 . 10^{-7} mol l^{-1}, c(HCl) = 0.5 mol l^{-1}. ○ *I*, Δ *III*, ■ *VIII*, □ *IX*, ◒ *X*, ● *X**

fact that the extraction of $HgCl_2$ into benzene alone (without reagent) proceeds least readily at a HCl concentration of 0.5 mol l^{-1} (ref.[5]).

The dependence of the distribution of mercury on the acidity of the aqueous phase at a constant concentration of selected reagents and at a constant ionic strength of I = 2.0 mol l^{-1}, adjusted with HCl and NaCl, is shown in Fig. 5. (The necessity to use a constant ionic strength followed from the fact that chloro complexes of mercury are relatively highly stable.) The minimum slope for reagents *III* and *X* is −2.0 ± 0.2. The dependences indicate that the extraction of mercury can be described by the pathway

$$Hg^{2+} + 2\,(HA)_{org} \rightleftharpoons (HgA_2)_{org} + 2\,H^+ \qquad (B)$$

with the extraction constant

$$K_{ex} = \frac{[HgA_2]_{org}\,[H^+]^2}{[Hg^{2+}]\,[HA]^2_{org}} = D_{Hg}\frac{[H^+]^2}{[HA]^2_{org}}\ . \qquad (2)$$

The distribution of mercury follows roughly the same sequence of reagents as the distribution of silver, the distribution ratios, however, are lower and correction must be made for the formation of chloro complexes[6].

In the aqueous phase the analytical concentration of mercury is

$$c_{Hg,\,aq} = [Hg^{2+}] + [HgCl^+] + [HgCl_2] + [HgCl_3^-] + [HgCl_4^{2-}] =$$
$$= [Hg^{2+}]\,(1 + \sum_{i=1}^{4} \beta_i\,[Cl^-]^i)\,, \qquad (3)$$

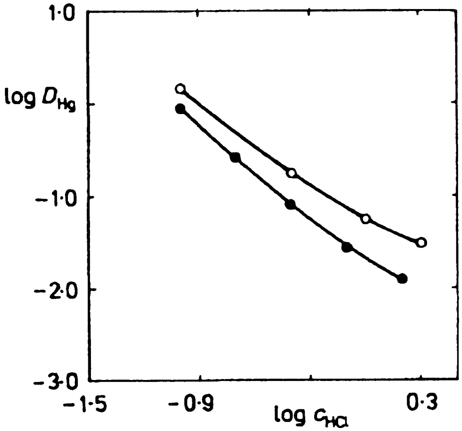


FIG. 5

Distribution of mercury in dependence on the starting hydrochloric acid concentration in the aqueous phase, I = 2.0 mol l^{-1}, c(Hg) = 1.89 . 10^{-7} mol l^{-1}, c(HA) (mol l^{-1}): 2 . 10^{-6} ○ *III*, 5 . 10^{-5} ● *X* where β_i's are the cumulative constants of chloro complexes of mercury, which must be taken into account in the calculation of K_{ex}. Using data of the tables[6], we obtain for $(1 + \Sigma\beta_i\,[Cl^-]^i)$ at $I = 0.5$ mol l^{-1} a value of $10^{13.6}$, so that the extraction constant is

$$K_{ex} = 10^{13.6}\,D_{Hg}\,[H^+]^2 / [HA]^2_{org} \; . \qquad (4)$$

Its values for the various reagents are given in Table II.

Distribution of the Remaining Metals

The distribution of some other metals forming divalent and trivalent cations, viz. Zn, Co, Cd, Sc, Eu and Tm, between the aqueous phase containing a mineral acid (see Experimental) and benzene solutions of reagents *IV* and *X* is shown in Fig. 6. The extraction proceeds more reluctantly than in the case of silver or mercury and the reagent concentration must be chosen higher than 1 . 10^{-2} mol l^{-1}. The data concerning the 50% extraction are included in Table I. Slope analysis suggests that the species passing into the organic phase are the uncharged ZnA_2, CoA_2, CdA_2 and LnA_3 complexes.

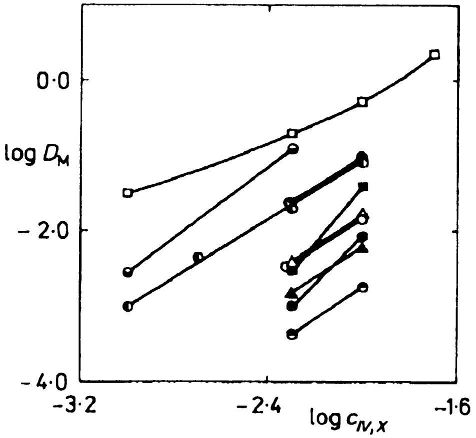


FIG. 6
Distribution of other metals in dependence on the starting reagent concentration in benzene. Acid: HCl for Co, Zn, $HClO_4$ otherwise; c(acid) = 0.1 mol l^{-1}. Reagent *IV* for □ Sc, ◒ Tm, ◐ Eu, △ Co, ○ Zn: reagent *X* for ⊙ Cd, ■ Sc, ● Eu, ▲ Co, ⊖ Zn

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Translated by P. Adámek.