SYNTHESIS AND EXTRACTION PROPERTIES OF ETHYLENEDIAMINODIALKYLPHOSPHONIC ACID ESTERS

UDC 542.91:542.61:547.1'118

T. Ya. Medved', M. V. Rudomino, V. N. Avilina, N. V. Churilina, K. F. Paraskevova, N. M. Dyatlova, and M. I. Kabachnik

The complexing selectivity of organophosphorus compounds, and more especially, of phosphorylated ethylenediamine derivatives containing $(HO)_2P(O)$, HOP(H)(O), HOP(R)(O) groups, is determined by the acid group and carbon-nitrogen chain structures [1-3].

It seemed of interest to study the extraction properties of those esters of the ethylenediaminodialkyl phosphonic acids (EDDPA) which are analogous to the organophosphorus complexes but contain completely blocked $(RO)_2P(O)$ groups. Compounds of the $(RO)_2P(O)CR'R"NHCH_2CH_2NHCR'R"P(O)(OR)_2$ type have four potential coordination centers per molecule, namely, the O atoms of the P=O phosphoryl groups and the N atoms.

Esters of the EDDPA (Table 1) were prepared by the method of [4, 5], condensing ethylenediamine with various carbonyl compounds and dialkylphophites

The products obtained were purified by chromatographing their benzene solutions on Al_2O_3 . The compounds themselves were transparent, almost colorless liquids, which could not be distilled even under high vacuum; they were insoluble in water. 5% ammonium carbonate, and solutions of acids and bases, but dissolved readily in organic solvents.

EXPERIMENTAL

<u>Preparation of Compounds (I)-(IV).</u> A quantity 0.5 mole of dialkylphosphite [6-8] and 0.5 mole ketone were added simultaneously and from separate funnels to 0.25 mole of ethylenediamine at 60°C. The resulting mixture was allowed to stand for 15 min, cooled. and extracted with 500 ml benzene. This solution was washed, first with 40 ml saturated K_2CO_3 solution, and then with 40 ml water, and dried over Na₂SO₄. The benzene was then evaporated off in vacuum, the residue taken up in five times its volume of abs. benzene, and the resulting solution chromatographed.

Octyl Ester of Ethylenediaminobenzylphosphonic Acid (V). A quantity 4.0 g, (0.017 mole) of N,N'-ethylenebis (benzylimine) was prepared by reacting 1.4 g ethylenediamine with 5 g benzaldehyde [9]; this was dissolved in 25 ml benzene and 11.1 g (0.034 mole) dioctylphosphite added dropwise to the agitated solution at 60°C [7]. The solution was held at 60°C for 30 min, cooled, washed with 10 ml of saturated K_2CO_3 solution and 10 ml

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Institute of Chemical Reagents and High-Purity Chemical Substances, Moscow. Translated from Izvestiya Akademii Nauk SSSR. Seriya Khimicheskaya, No. 11, pp. 2445-2450, November, 1976. Original article submitted October 1. 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

Picrates
Their
and
Acids
hosphonic
lialkylpl
iaminod
hylened
of Et
Esters (
TABLE 1.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Calculated, %	Ŀ	11.7	6,0	10,6 5,9	5,2 7,2	9,2 5,5	7,3
		z	5,3	11,0	$^{4,8}_{10,8}$	3,7 9,3	$^{4,2}_{10,1}$	3.3 8 9
		п	10,3	6,0	$ \frac{10.7}{6,6} $	$^{11,5}_{7,7}$	$^{11,2}_{7,2}$	$^{10,2}_{7,1}$
		υ	54.5	42,2	57,5 46,1	64,3 51,5	61,0 $49,1$	67,9 55,1
	Molecular formula		C ₉₄ H ₅₄ N ₉ O ₆ P ₉	C36H60N8O20P2	$C_{26}H_{62}N_{2}O_6P_2$ $C_{40}H_{68}N_8O_{20}P_2$	C40H86N2O6P2 C52H92N6O20P2	$C_{34}H_{74}N_{2}O_{6}P_{2}C_{46}H_{80}N_{8}O_{20}P_{2}$	C48H86N2O6P2 C60H92N8O20P2
		Ŀ	11.6	6,0	10,6 5,3	7,8 4,7	8.0 8.0	6,9 4,1
	id, <i>%</i>	z	5.7	11,5	10,9 10,9	3,7 9,0	4,6 10,4	3,5 9,0
	Foun	ш	10.2	6,2	10,9 6,8	11,7 7,8	11,3 7,6	10,4 7,2
		υ	54,4	42,5	56,8 46,0	64,7 51,7	60,7 49,2	67 , 6 55,0
	1, ²⁰ D		1,4590	1	1,4560	1,4579	1,4605	1,4881
	d_A^{20}		1,0097	-	0,9961	0,9464	0,9772	0,9948
	mp, °C (from alcohol)			151, 5 - 152	$\frac{-}{136-138}$	124 - 126	100 - 102	-146-148
	Yıeld,		72		86	53	89	82
	R"		CII ₃	1	CH_3	CII ₃	C ₆ II ₁₃	C ₆ H ₅
	B,		CH _a	Dipicrate	Dipicrate	Dipicrate	Dipicrate	II Dipicrate
	a,		$C_{A}H_{a}$	•	C ₆ H ₁₁	СцП ₁₇	C4H9	C ₈ H ₁₇
	Com- pound		(1)		(11)	(111)	(IV)	(Š

TABLE 2. Distribution Coefficients (D) for the Extraction of Au(III) by Compound (I) in Solvents of Various Dielectric Constants (E)

lg D	$\begin{array}{c} 1,38\\ 1,49\\ 1,54\\ 1,98\\ 1,98\end{array}$
<u>е</u>	$\begin{array}{c} 2.57 \\ 2.57 \\ 4.81 \\ 5.62 \\ 10, 36 \\ 10, 36 \end{array}$
Solvent	o-Xylol Chloroform Chlorobenzene 1,2-Dichloro- ethane
lg D	1,15 1,24 1,28 1,28 1,33
ω	2,28
Solvent	Heptane Gyclohexane COla Benzene Toluene

water, and then dried over Na_2SO_4 . The benzene was evaporated off in vacuum. Yield of (V), 12.4 g (82%). The compound crystallized on standing.

Study of the Extraction Properties of Compounds (I)-(V). Solutions containing the extractants at concentrations in the $5 \cdot 10^{-1}$ to $1 \cdot 10^{-4}$ M range (Table 2) were prepared by precision weighing. The Au(III) concentration was varied over the 10^{-4} - 10^{-6} M range, determination being based on radiochemical assay of the ¹⁹⁸Au isotope introduced into the solution as HAuCl₄. The radiochemical purity of the isotope was checked through the γ spectrum. Preliminary experiments showed that aqueous and organic phases could be brought into extractional equilibrium by 15-min agitation on a mechanical vibrator at $20 \pm 1^{\circ}$ C. After layer separation (5 min), 0.5-min aliquots were taken from each phase for specific activity determinations. The radioactivity (γ radiation) was measured with an LAS system, using a scintillation counter and a NaI monocrystal. The Au(III) distribution coefficient was determined from the ratio of the specific activities of the organic and aqueous phases, correction being made for background noise.

Experiments on the extraction of rare-earth compounds were carried out with solutions containing Nd (III), Ce (III) and Ce (IV) salts at $1.5 \cdot 10^{-4}$ M concentration, working with $1 \cdot 10^{-2}$ M solutions of the extractant in chloroform. The pH values of the Nd (III) and Ce (III) solutions were adjusted with the aid of ammonium acetate buffers; those of the Ce (IV) solutions, with 0.1 N H₂SO₄ and 0.1 N NaOH. The ionic strength of each solution was held at $\mu = 0.1$ by addition of 0.1 M NaClO₄ to the Nd (III) and Ce (III) solutions and 0.1 M (NH₄)₂SO₄ to the Ce (IV) solution. The concentrations of the rare-earth ions were determined spectrophotometrically, using arsenazo III [10]. Equilibrium was established under the same conditions as for the work on Au (III).

DISCUSSION OF RESULTS

It is seen from Fig. 1 that the distribution coefficient for Au(III) extraction by 0.1 M solutions of (I)-(V) in chloroform increased with increasing HCl concentration, passed through a maximum at 2-4 M HCl, and then diminished, the situation here being similar to that met in the extraction of Au(III) by butyl phosphate [11]. The curve forms indicated that the extraction mechanism was the same for each of the compounds under study here. The difference in the positioning of the curves with respect to the axis of ordinates suggested that the extractional capacity was fixed by the nature of the substituents, in the ester grouping and at the C atom joining the N and the P atoms in the molecule.

In the (I)-(III) series ($\mathbb{R}^{1} = \mathbb{R}^{m} = \mathbb{C}H_{3}$), it was observed that the extracting capacity fell off somewhat with increasing size of the ester radical: (I) ($\mathbb{C}_{4}H_{9}$) > (II) ($\mathbb{C}_{5}H_{11}$) > (III) ($\mathbb{C}_{8}H_{17}$), clearly because of steric hindrances arising, in the last two instances, from the close proximity of the ester radical and the branched isopropyl group [12].



Fig. 1. Variation of the logarithm of the distribution coefficient for Au(III) extraction from HCl solution by compounds (I-(V) with the aqueous phase composition. $[HAucl]_4 = 1 \cdot 10^{-4}$, $[(I)-(V)] = 1 \cdot 10^{-1}$ M; solvent, chloroform; $V_{org} = V_{ag} = 2.0$ ml.

Fig. 2. Bilogarithmic plot of the distribution coefficient for Au(III) extraction from 2 M HCl by compound (I) in CHCl₃ against the extractant concentration in the organic phase. [HAuCl₄], M: 1) $1 \cdot 10^{-4}$; 2) $1 \cdot 10^{-5}$; 3) $1 \cdot 10^{-6}$.



Fig. 3. Variation of the reextraction of Au(III) from $CHCl_3$ solutions of compound (I) with the concentration of the reextracting agent in the aqueous phase: 1) HCl, 2) HNO₃; 3) H₂SO₄; 4) NaOH; 5) NH₄OH. [I] = $1 \cdot 10^{-2}$, [HAuCl₄] = $1 \cdot 10^{-4}$ M.

Fig. 4. Variation of the rare-earth ion extraction by (III) solutions with the pH of the aqueous phase; solvent, CHCl₃. Curve 1) [III] = $1 \cdot 10^{-2}$ M; 2) [III] = $1 \cdot 10^{-3}$ M. A. Nd(III), m: a) $1.5 \cdot 10^{-4}$; b) $3.8 \cdot 10^{-5}$. B. Ce(III), m: a) $1.5 \cdot 10^{-4}$; b) $3.8 \cdot 10^{-5}$. B. Ce(IV), N: a) $1.3 \cdot 10^{-4}$; b) $4.4 \cdot 10^{-5}$.

On the other hand, the extracting capacity of (IV) $(R' = CH_3, R'' = C_6H_{13})$ was considerably higher than that of (I) $(R' = R'' = CH_3)$, and the extracting capacity of (V) was higher still.

Comparison of our results with those reported in [13] made it clear that our Au(III) distribution coefficients for extraction with $5 \cdot 10^{-1}$ to $1 \cdot 10^{-4}$ M solutions of the compounds in question here were higher by 1.5-2 orders than those for extraction by tributyl phosphate.

The extraction of Au(III) by solutions of (I) was studied in greater detail. Following the method of equilibrium displacement proposed in [14] it was shown (Fig. 2) that a 1:1 metal-to-ligand complex was extracted out when Au(III) solutions at 10^{-4} - 10^{-6} M concentration in 2 M HCl are treated with $5 \cdot 10^{-1}$ to $1 \cdot 10^{-4}$ M solutions of compound (I) in chloroform.

It is seen from Table 2 that the distribution coefficient increased with increasing dielectric constant of the solvent, the best solvents, in this respect, being chloroform, chlorobenzene, and 1,2-dichloroethane. Similar relations have been reported from work on Au(III) extraction by various pyrazolone derivatives [15].

It was also possible to reextract the Au(III) from the organic phase with 0.1-10 M solutions of mineral acids, NaOH, and NH₄OH (Fig. 3). Single-step reextraction of Au(III) could also be carried out with 1-10 M NH₄OH and with 9-10 M HNO₃.

The pH of the medium was the most significant factor in fixing the effectiveness of rare-earth compound extraction by (III) solutions. As the curves of Fig. 4 indicate, there was a narrow range of pH values over which such extraction was almost complete (7.5-8.5). The fact that the efficiency of extraction was independent of the rare-earth ion concentration in the aqueous phase was indication that polynuclear complexes were not formed in the extraction process. Reducing the concentration from $1 \cdot 10^{-2}$ to $1 \cdot 10^{-3}$ M displaced the extraction curve toward higher pH values and reduced the optimal pH range. The falloff in the extraction curve at pH values in excess of 9 could have resulted from partial saponification of the ester group, or the formation of water-soluble complexes, or even hydrolysis of the metal ion complex-former.

CONCLUSIONS

1. A new group of ethylenediaminodialkylphosphonic acid esters and higher alcohols has been synthesized.

2. Study has been made of the extraction of Au(III) from hydrochloric acid solution by the esters of these acids. It has been shown that the extract is a 1:1 metal-to-ligand complex. The distribution coefficient of the Au(III) extraction increases with the dielectric constant of the extracting solvent. It has also been established that the Au(III) can be reextracted out of the organic phase by NH₃ or HNO₃.

3. Study has been made of the extraction of Nd(III), Ce(III) and Ce(IV) ions by the octyl ester of ethylenediaminodiisopropylphosphonic acid. Extraction of these ions can be carried out almost quantitatively at pH values in the 7.5-8.5 interval.

LITERATURE CITED

- 1. N. M. Dyatlova, M. I. Kabachnik, T. Ya. Medved', Yu. F. Belugin, and M. V. Rudomino, Dokl. Akad. Nauk SSSR, 161, 607 (1965).
- 2. T. Ya. Medvev', N. M. Dyatlova, M. V. Rudomino, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1211 (1968).
- 3. N. M. Dyatlova, T. Ya. Medved', M. V. Rudomino, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 815 (1970).
- 4. M. I. Kabachnik, T. Ya. Medved', G. K. Kozlova, V. S. Balabukha, M. M. Senyavin, and L. I. Tikhonova. Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1070 (1958).
- 5. T. Ya. Medved', M. V. Rudomino, E. A. Mironova, V. S. Balabukha, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 351 (1967).
- 6. B. A. Arbuzov and G. I. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 617 (1947).
- 7. F. L. Maklyaev, N. K. Bliznyuk, and G. I. Eremin, Zh. Obshch. Khim., 30, 4053 (1960).
- 8. D. Ramaswanni and E. R. Kirch, J. Am. Chem. Soc., 75, 1763 (1963).
- 9. C. Mason, Ber., 20, 270 (1887).
- 10. S. B. Savvin, Arsenazo III. Methods for Photometric Determination of Rare and Active Elements [in Russian], Atomizdat (1966).
- 11. T. Schimori, K. Watanable, and E. Nakamura, Bull. Chem. Soc. Japan, 33, 636 (1960).
- 12. A. M. Rozen and Z. I. Nikolotova, Zh. Neorg. Khim., 9, 1725 (1964).
- 13. H. Specker and W. Pappert, Z. Anorg. Alleg. Chem., 341, 287 (1965).
- 14. Yu. A. Zolotov and I. V. Seryakova, Proc. Commission on Analytical Chemistry of the Academy of Sciences of the USSR [in Russian], Vol. 17, Nauka (1969).
- 15. V. K. Akimov, A. I. Busev and L. V. Shubashevich, Zh. Analit. Khim., 28, 389 (1973).