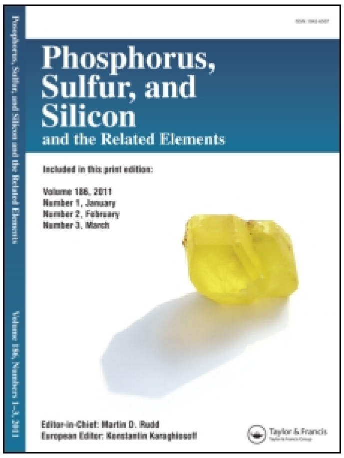

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BI- AND TRIDENTATE ORGANOPHOSPHORUS COMPOUNDS FOR EXTRACTION AND COMPLEXATION OF METAL IONS

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Abstract. Studies of structure-reactivity relations were carried out in solvent extraction and coordination chemistry of metal ions M^{z+} {Na(I), Mg(II), Ca(II), Sr(II), Ba(II), Ln(III) (Sc, Y, La...Lu), Hf(IV), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), Tl(I), Pb(II), and Bi(III)} with 38 bi- and tridentate μ-imido organophosphorus compounds with oxygen and sulfur donor atoms. These compounds are Brønsted acids, HA, and form chelate complexes MA_z in most cases. Different modes of coordination are observed. The extraction of metal ions depends not on only on the set of donor atoms, and the acidity and dimerization constant of the organophosphorus compound. In some cases steric effects are dominant. It was also observed an important influence of the diluent.

Key words: μ-Imido-diphosphates; μ-imido-thiodiphosphates; μ-imido-dithiodiphosphates, di-μ-imido-triphosphates, N-thiophosphoryl thioureas; solvent extraction; coordination chemistry.

INTRODUCTION

Starting with the tetraphenyl μ-imido-diphosphate **1a** [1-3] it has been shown, that μ-imido-diphosphates are effective reagents for complexation and liquid-liquid extraction of metal ions. The following compounds:
$(RO)_2P(X)\text{-}NH\text{-}P(Y)(OR^1)_2$ (X,Y = O: **1a-e**, **1g-h**; X = O, Y = S: **2a-d**; X,Y = S: **3a**, **3b**, **3d-f**; R,R^1= Ph: **a**; R,R^1= 2-Me-Ph: **b**; R,R^1= 3-Me-Ph: **c**; R,R^1= 4-Me-Ph: **d**; R = 4-Me-Ph, R^1= Ph: **e**; R = Ph, R^1= 2-Me-Ph: **f**; R,R^1= Oc: **g**; R,R^1= Hex: **h**), $(PhO)_2P(O)\text{-}NH\text{-}P(O)(OPh)OH$ **4**, $(RO)_2P(O)\text{-}NH\text{-}P(O)(OR)NH_2$ **5**, $(RO)_2P(X)\text{-}NH\text{-}P(X)(OR)\text{-}NH\text{-}P(X)(OR^1)_2$ (X = O: **6a**, **6c**, **6e**; X = S: **7a**), $Ph_2P(S)\text{-}NH\text{-}P(S)Ph_2$ **8**, $(PhO)_2(S)\text{-}NH\text{-}C(CH_3)\text{=}CH\text{-}CN$ **9**, $(PhO)_2P(S)\text{-}NH\text{-}C(S)\text{-}NR^2R^3$ **10i-u** (R^2= R^3= Et: **i**, *n*-Pr: **k**, *i*-Pr: **l**, *n*-Bu: **m**, *i*-Bu: **n**, *cyc*-Hex: **o**, Oc: **p**, Ph: **q**; R^2= Me, R^3= Ph: **r**; R^2= H, R^3= *t*-Bu: s, R^2= H, *n*-Hep: **t**, R^2= H, 4-Me-Ph: **u**)

were synthesized and tested to extend systematic studies of structure - reactivity relations in solvent extraction of Na(I), Mg(II), Ca(II), Sr(II), Ba(II), Ln(III) (Sc, Y, La...Lu), Hf(IV), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Ag(I), Au(III), Zn(II), Cd(II), Hg(II), Tl(I), Pb(II), and Bi(III).

RESULTS AND DISCUSSION

All these μ-imido compounds are Brønsted acids, HA or H_2A. Some acidity exponents pK_a were determined by potentiometric titration in ethylenglycole monomethylether/ water (4:1). The pK_a values are 2.4, 2.7, 2.8, 2.6, 2.8, 3.0, 3.0, 3.2, (2.2 and 10.8), 4.4, (2.4 and 9.4), and 9.9 for **1a**, **1b**, **1d**, **1e**, **2a**, **2b**, **2c**, **3a**, **3e**, **4**, **5**, **6e**, and **9**, respectively. The acidity of **1** - **6** increases with rising electronegativity of the substituents. Sulfur donor atoms decrease the acidity.

The tetraaryl esters of the derivatives of the μ-imido-diphosphoric acid form dimers via hydrogen bonds as shown by X-ray crystal structure analysis of **1a** [4] , **1b**, **2b**, **2c**, **2d** [5], and **3a** [6]. Dimers are also formed in nonpolar diluents. The dimerization constants K_{dim} were determined in benzene for some compounds (log K_{dim}: 3.3(3), 4.6(5), 2.8(5), 2.2(3) for **1a**, **1b**, **1d**, and **2a**, respectively). No dimerization was found for **3a** in benzene.

Most of the compounds **1-10** form neutral chelate complexes according to equation (1) and (2) by extraction of metal ions from aqueous solution.

$$M^{z+}_{(aq)} + z\,HA_{(org)} \rightleftharpoons MA_{z(org)} + z\,H^{+}_{(aq)} \quad (1)$$

$$M^{z+}_{(aq)} + z/2\,HA_{2(org)} \rightleftharpoons MA_{z(org)} + z\,H^{+}_{(aq)} \quad (2)$$

The mode of coordination is different. While Yb^{3+} is surrounded by six oxygen atoms in form of a slightly distorted octahedron in the complex with **1a** [7], Pd^{2+} and Ni^{2+} are coordinated via 4 sulfur atoms in a square planar complex with **3a** [6], and **10k** [8], respectively. Six-membered chelate rings are formed in both complexes. Four-membered chelate rings are observed in the square planar complex of Pd^{2+} with **2a**. However the coordination of the metal ion occurs via sulfur and nitrogen atoms [9]. Monovalent cations show an interesting self-organization effect. Oligomers with an inorganic nucleus (FIGURE 1) and an organic shell are formed. A three-nuclear copper(I) complex is yielded in the reaction of **10** with copper(II) [10]. Sodium forms with **1a** a six-nuclear complex in the crystal [11] as well as in benzene.

The slope analysis of the dependence of distribution ratios D on the concentration of HA in the organic phase and mineral acid in the aqueous phase shows that complexes MA_z are formed in the organic phase with Na(I), Mg(II), Ca(II), Sr(II), Ba(II), Ln(III) (Sc, Y, La...Lu), Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Tl(I), Pb(II), and Bi(III). Silver yielded AgA(HA)[13].

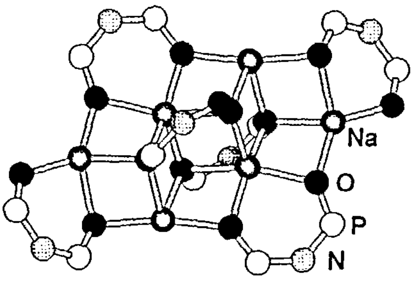

FIGURE 1 Nucleus of $\{Na[(C_6H_5O)_2PO]_2N\}_6$

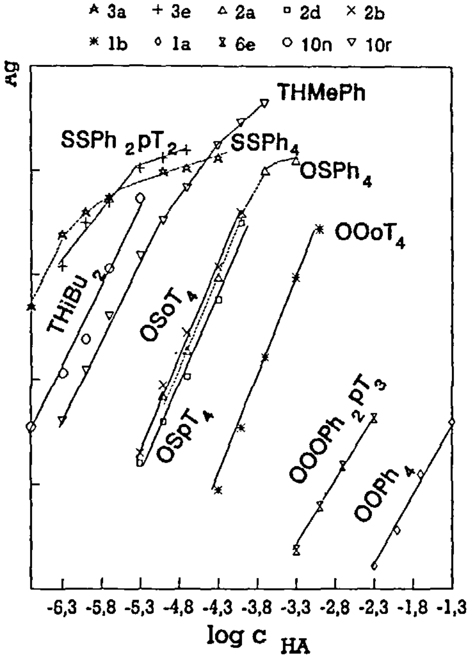

FIGURE 2 Log D of silver at 1 M HNO_3 vs. initial extractant molarity in benzene ($c_{Ag} = 6 \times 10^{-8}$ M)

The HSAB concept is reflected very well in the extraction of different metal ions in dependence on the set of donor atoms of the extractant. The strength of extraction of e.g. Ag(I) (see FIGURE 2) and Hg(II) decreases with the set of donor atoms SS > OS> OO. The corresponding sequences are OS > OO > SS, and OO >> OS > SS for Zn(II) and typical hard metal ions (e.g. rare earths, alkaline earth metals), respectively. For a given set the D values rises as a rule with increasing acidity of HA The highest strength of extraction was observed for silver. It is extracted quantitatively (log D > 4) from 1.0 M HNO_3 with **8**, even if the concentration of HA in the organic phase is only 10^{-7} M. D values decrease in the sequence of extractants **8** >> **3a** > **3e** > **10n** > **10r** >> **2b** > **2a** > **2d** >> **1b** > **6e**> **1a**. Steric hinderance results in different sequences of extractants for smaller and bigger metal ions (e.g.**1a** > **1d** > **6e** > **1b** > **2d** > **2c** > **2b** > **2a** > **3a** for Sc(III) and **6e** ≈ **4** > **5** > **1a** > **1d**>> **1b**> **3a** > **2c** > **3e** > **2a** for Ce(III). The small Sc^{3+} is not able to coordinate all the nine oxygen donor atoms of **6e**.) Distribution ratios of rare earth ions drop as well as separation factors in the sequence **1a** > **1g** > **1h**.

The kind of the organic diluent has also a remarkable strong influence on the strength of extraction of e.g. Sc(III), Tm(III), and Eu(III) with **1a** or **10a** [14]. D values of e.g. Yb^{3+} drop under given conditions by four orders of magnitude using methyl-*iso*-butyl-ketone instead of benzene as a diluent for **1a**.

The results of this paper have shown, that the extraction behaviour of an organophosphorus compound depends on a lot of factors. Some of them are well understood. But it needs further investigations to obtain a more realistic picture for an aimed design of an extractant.

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