

Short communication

# Solvent Extraction of Calcium and Strontium into Nitrobenzene by Using a Synergistic Mixture of Hydrogen Dicarbolylcobaltate and 2,6-(Diphenylphosphino)Pyridine Dioxide

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## Abstract

Solvent extraction of microamounts of calcium and strontium by a nitrobenzene solution of hydrogen dicarbolylcobaltate ( $H^+B^-$ ) in the presence of 2,6-(diphenylphosphino)pyridine dioxide (DPPPDO, L) has been investigated. The equilibrium data have been explained assuming that the species  $HL^+$ ,  $HL_2^+$ ,  $CaL_2^{2+}$ ,  $CaL_3^{2+}$ ,  $SrL_2^{2+}$ ,  $SrL_3^{2+}$  and  $SrL_4^{2+}$  are extracted into the organic phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

**Keywords:** Calcium, strontium, hydrogen dicarbolylcobaltate, 2,6-(diphenylphosphino)pyridine dioxide, water-nitrobenzene system, extraction and stability constants

## 1. Introduction

The dicarbolylcobaltate anion<sup>1</sup> and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially  $Cs^+$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Eu^{3+}$  and  $Am^{3+}$ ) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,<sup>2–29</sup> and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.<sup>30,31</sup>

Bidentate phosphonates, phosphine oxides and malonamides have been intensively studied for the extraction

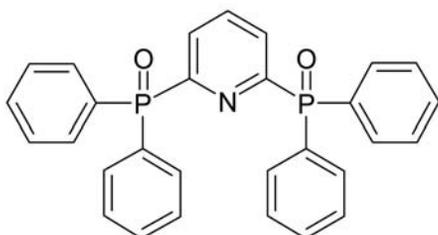
of trivalent lanthanides and actinides from acidic media.<sup>32–34</sup> A process using octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (i.e. “classical” CMPO) and called TRUEX was apparently used in the United States,<sup>32</sup> whereas malonic diamides ( $RR'NCO)_2CHR''$  (DI-AMEX) were proposed in France.<sup>33</sup>

Recently, extractive properties of a synergistic mixture of hydrogen dicarbolylcobaltate ( $H^+B^-$ )<sup>1</sup> and 2,6-(diphenylphosphino)pyridine dioxide (DPPPDO, L; see Scheme 1) toward  $Eu^{3+}$  have been investigated in the water-nitrobenzene system.<sup>35</sup> On the other hand, in the current work, the solvent extraction of microamounts of calcium and strontium by a nitrobenzene solution of the mentioned synergistic mixture was studied. We intended

to find the composition of the species in the organic phase and to determine the corresponding equilibrium constants.

## 2. Experimental

Preparation of 2,6-(diphenylphosphino)pyridine dioxide (DPPDO, L; see Scheme 1) was presented in Ref. 36. Cesium dicarbollylcobaltate,  $\text{Cs}^+\text{B}^-$ , was synthesized by means of the method published by Hawthorne et al.<sup>37</sup> A nitrobenzene solution of hydrogen dicarbollylcobaltate ( $\text{H}^+\text{B}^-$ )<sup>1</sup> was prepared from  $\text{Cs}^+\text{B}^-$  by the procedure described elsewhere.<sup>38</sup> The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclides  $^{45}\text{Ca}^{2+}$  and  $^{85}\text{Sr}^{2+}$  (DuPont, Belgium) were of standard radiochemical purity.



**Scheme 1.** Structural formula of 2,6-(diphenylphosphino)pyridine dioxide (abbrev. DPPDO or L, respectively).

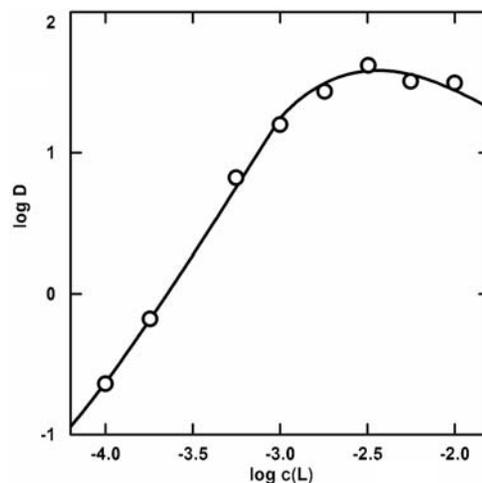
The extraction experiments in the two-phase water–HCl– $\text{M}^{2+}$  (microamounts;  $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$ )–nitrobenzene–DPPDO– $\text{H}^+\text{B}^-$  systems were performed in 10 mL glass test-tubes with polyethylene stoppers, using 2 mL of each phase. The test-tubes filled with the solutions were shaken for 2 hours at  $25 \pm 1$  °C, using a laboratory shaker. Under these conditions, the equilibria in the systems under study were established after approximately 20 min of shaking. Then the phases were separated by centrifugation. In the case of the systems involving  $^{45}\text{Ca}^{2+}$ , after evaporating aliquots (1 mL) of the respective phases on Al plates, their  $\beta$ -activities were measured by using the apparatus NRB-213 (Tesla Přemyšlení, Czech Republic). On the other hand, in the case of the systems with  $^{85}\text{Sr}^{2+}$ , 1 mL samples were taken from each phase and their  $\gamma$ -activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a  $\gamma$ -analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of calcium and strontium,  $D$ , were determined as the ratios of the corresponding measured radioactivities of  $^{45}\text{Ca}^{2+}$  and  $^{85}\text{Sr}^{2+}$  in the nitrobenzene and aqueous samples.

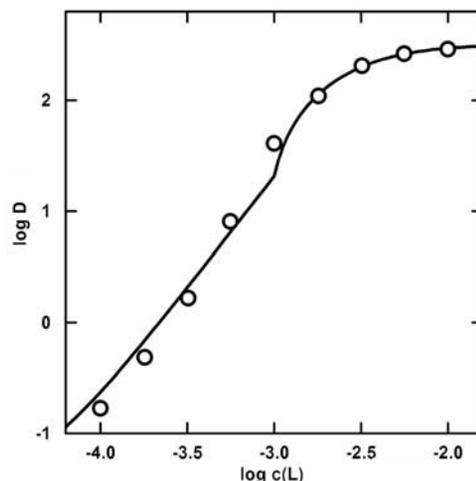
## 3. Results and Discussion

The dependences of the logarithm of the calcium and strontium distribution ratios ( $\log D$ ) on the logarithm

of the numerical value of the total (analytical) concentration of the DPPDO ligand in the initial nitrobenzene phase,  $\log c(\text{L})$ , are given in Figures 1 and 2, respectively. The initial concentration of hydrogen dicarbollylcobaltate in the organic phase,  $c_{\text{B}} = 0.001$  mol/L, as well as the initial concentration of HCl in the aqueous phase,  $c(\text{HCl}) = 0.01$  mol/L, are always related to the volume of one phase.



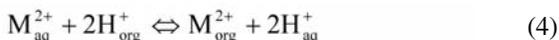
**Figure 1.**  $\log D$  as a function of  $\log c(\text{L})$ , where L is DPPDO, for the water–HCl– $\text{Ca}^{2+}$  (microamounts)–nitrobenzene–DPPDO– $\text{H}^+\text{B}^-$  system;  $c(\text{HCl}) = 0.01$  mol/L,  $c_{\text{B}} = 0.001$  mol/L. The curve was calculated using the constants given in Table 3.



**Figure 2.**  $\log D$  as a function of  $\log c(\text{L})$ , where L is DPPDO, for the water–HCl– $\text{Sr}^{2+}$  (microamounts)–nitrobenzene–DPPDO– $\text{H}^+\text{B}^-$  system;  $c(\text{HCl}) = 0.01$  mol/L,  $c_{\text{B}} = 0.001$  mol/L. The curve was calculated using the constants given in Table 4.

With respect to the results of previous papers,<sup>3,9,14,28,29</sup> the considered water–HCl– $\text{M}^{2+}$  (microamounts;  $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$ )–nitrobenzene–DPPDO(L)– $\text{H}^+\text{B}^-$  systems can be described by the set of reactions:





to which the following equilibrium constants correspond:

$$K_D = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \quad (6)$$

$$\beta(\text{HL}^+_{\text{org}}) = \frac{[\text{HL}^+_{\text{org}}]}{[\text{H}^+_{\text{org}}][\text{L}_{\text{org}}]} \quad (7)$$

$$\beta(\text{HL}^+_{2,\text{org}}) = \frac{[\text{HL}^+_{2,\text{org}}]}{[\text{H}^+_{\text{org}}][\text{L}_{\text{org}}]^2} \quad (8)$$

$$K_{\text{ex}}(\text{M}^{2+}_{\text{org}}) = \frac{[\text{M}^{2+}_{\text{org}}][\text{H}^+_{\text{aq}}]^2}{[\text{M}^{2+}_{\text{aq}}][\text{H}^+_{\text{org}}]^2} \quad (9)$$

$$K_{\text{ex}}(\text{ML}^{2+}_{n,\text{org}}) = \frac{[\text{ML}^{2+}_{n,\text{org}}][\text{H}^+_{\text{aq}}]^2}{[\text{M}^{2+}_{\text{aq}}][\text{L}_{\text{org}}]^n[\text{H}^+_{\text{org}}]^2} \quad (10)$$

The subscripts “aq” and “org” denote the aqueous and organic phases, respectively.

A subroutine UBBE, based on the relations given above, the mass balance of the DPPPDO ligand and the electroneutrality conditions in both phases of the system under consideration, was formulated<sup>39,40</sup> and introduced into a more general least-squares minimizing program LETAGROP<sup>41</sup> used for determination of the “best” values of the extraction constants  $K_{\text{ex}}(\text{ML}^{2+}_{n,\text{org}})$  ( $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$ ;  $\text{L} = \text{DPPPDO}$ ). The minimum of the sum of errors in log D, i.e., the minimum of the expression

$$U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (11)$$

was sought.

The values  $\log K_D = 2.38$ ,<sup>35</sup>  $\log \beta(\text{HL}^+_{\text{org}}) = 9.45$ ,<sup>35</sup>  $\log \beta(\text{HL}^+_{2,\text{org}}) = 11.99$ ,<sup>35</sup>  $\log K_{\text{ex}}(\text{Ca}^{2+}_{\text{org}}) = 0.2$ <sup>42</sup> and  $\log K_{\text{ex}}(\text{Sr}^{2+}_{\text{org}}) = 0.7$ <sup>39</sup> were used for the respective calculations. The results are listed in Tables 1 and 2. From these tables it is evident that the extraction data can be best explained assuming the complexes  $\text{CaL}^{2+}_2$ ,  $\text{CaL}^{2+}_3$ ,  $\text{SrL}^{2+}_2$ ,  $\text{SrL}^{2+}_3$  and  $\text{SrL}^{2+}_4$  ( $\text{L} = \text{DPPPDO}$ ) to be extracted into the nitrobenzene phase.

Knowing the values  $\log K_{\text{ex}}(\text{Ca}^{2+}_{\text{org}}) = 0.2$ <sup>42</sup> and  $\log K_{\text{ex}}(\text{Sr}^{2+}_{\text{org}}) = 0.7$ ,<sup>39</sup> as well as the extraction constants  $\log K_{\text{ex}}(\text{CaL}^{2+}_{2,\text{org}}) = 22.19$ ,  $\log K_{\text{ex}}(\text{CaL}^{2+}_{3,\text{org}}) = 26.56$ ,  $\log K_{\text{ex}}(\text{SrL}^{2+}_{2,\text{org}}) = 22.21$ ,  $\log K_{\text{ex}}(\text{SrL}^{2+}_{3,\text{org}}) = 26.23$  and  $\log K_{\text{ex}}(\text{SrL}^{2+}_{4,\text{org}}) = 28.48$  determined here (see Tables 1 and 2), the stability constants of the complexes  $\text{ML}^{2+}_2$ ,  $\text{ML}^{2+}_3$  and  $\text{ML}^{2+}_4$  ( $\text{M}^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}$ ;  $\text{L} = \text{DPPPDO}$ ) in the organic phase defined as

**Table 1.** Comparison of various models of calcium extraction from aqueous solution of HCl by nitrobenzene solution of  $\text{H}^+\text{B}^-$  in the presence of DPPPDO.

Calcium complexes in the organic phase	$\log K_{\text{ex}}^a$	$U^b$
$\text{CaL}^{2+}_2$	22.58 (22.92)	2.15
$\text{CaL}^{2+}_3$	26.21 (27.05)	29.13
$\text{CaL}^{2+}_4$	29.55 (30.51)	57.08
$\text{CaL}^{2+}_2, \text{CaL}^{2+}_3$	$22.19 \pm 0.09, 25.56 \pm 0.12$	0.02
$\text{CaL}^{2+}_3, \text{CaL}^{2+}_4$	Transformed to $\text{CaL}^{2+}_3$	
$\text{CaL}^{2+}_2, \text{CaL}^{2+}_3, \text{CaL}^{2+}_4$	Transformed to $\text{CaL}^{2+}_2, \text{CaL}^{2+}_3$	

<sup>a</sup> The values of the extraction constants are given for each complex. The reliability interval of the constants is given as  $3\sigma(K)$ , where  $\sigma(K)$  is the standard deviation of the constant K.<sup>41</sup> These values are given in the logarithmic scale using the approximate expression  $\log K \pm \{\log[K + 1.5\sigma(K)] - \log[K - 1.5\sigma(K)]\}$ . For  $\sigma(K) > 0.2 K$ , the previous expression is not valid and then only the upper limit is given in the parentheses in the form of  $\log K(\log[K + 3\sigma(K)])$ .<sup>41</sup>

<sup>b</sup> The error-square sum  $U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2$ .

**Table 2.** Comparison of various models of strontium extraction from aqueous solution of HCl by nitrobenzene solution of  $\text{H}^+\text{B}^-$  in the presence of DPPPDO.

Strontium complexes in the organic phase	$\log K_{\text{ex}}^a$	$U^b$
$\text{SrL}^{2+}_2$	23.06 (23.60)	7.16
$\text{SrL}^{2+}_3$	26.93 (27.70)	19.90
$\text{SrL}^{2+}_4$	30.26 (31.15)	45.08
$\text{SrL}^{2+}_2, \text{SrL}^{2+}_3$	$22.21 \pm 0.24, 26.43 (26.64)$	0.42
$\text{SrL}^{2+}_3, \text{SrL}^{2+}_4$	Transformed to $\text{SrL}^{2+}_3$	
$\text{SrL}^{2+}_2, \text{SrL}^{2+}_3, \text{SrL}^{2+}_4$	$22.21 \pm 0.22, 26.23 (26.57), 28.48 (28.87)$	0.03

<sup>a</sup> See Table 1, footnote a. <sup>b</sup> See Table 1, footnote b.

$$\beta(\text{ML}^{2+}_{2,\text{org}}) = \frac{[\text{ML}^{2+}_{2,\text{org}}]}{[\text{M}^{2+}_{\text{org}}][\text{L}_{\text{org}}]^2} \quad (12)$$

$$\beta(\text{ML}^{2+}_{3,\text{org}}) = \frac{[\text{ML}^{2+}_{3,\text{org}}]}{[\text{M}^{2+}_{\text{org}}][\text{L}_{\text{org}}]^3} \quad (13)$$

$$\beta(\text{ML}^{2+}_{4,\text{org}}) = \frac{[\text{ML}^{2+}_{4,\text{org}}]}{[\text{M}^{2+}_{\text{org}}][\text{L}_{\text{org}}]^4} \quad (14)$$

can be evaluated applying the following simple relations:

$$\log \beta(\text{ML}^{2+}_{2,\text{org}}) = \log K_{\text{ex}}(\text{ML}^{2+}_{2,\text{org}}) - \log K_{\text{ex}}(\text{M}^{2+}_{\text{org}}) \quad (15)$$

$$\log \beta(\text{ML}^{2+}_{3,\text{org}}) = \log K_{\text{ex}}(\text{ML}^{2+}_{3,\text{org}}) - \log K_{\text{ex}}(\text{M}^{2+}_{\text{org}}) \quad (16)$$

$$\log \beta(\text{ML}^{2+}_{4,\text{org}}) = \log K_{\text{ex}}(\text{ML}^{2+}_{4,\text{org}}) - \log K_{\text{ex}}(\text{M}^{2+}_{\text{org}}) \quad (17)$$

The respective equilibrium constants are summarized in Tables 3 and 4.

**Table 3.** Equilibrium constants in the water – HCl– Ca<sup>2+</sup> (microamounts) – nitrobenzene – DPPPDO – H<sup>+</sup>B<sup>-</sup> system.

Equilibrium	log K
$L_{aq} \rightleftharpoons L_{org}$	2.38 <sup>a</sup>
$H^+_{org} + L_{org} \rightleftharpoons HL^+_{org}$	9.45 <sup>a</sup>
$H^+_{org} + 2L_{org} \rightleftharpoons HL^+_{2,org}$	11.99 <sup>a</sup>
$Ca^{2+}_{aq} + 2H^+_{org} \rightleftharpoons Ca^{2+}_{org} + 2H^+_{aq}$	0.2 <sup>b</sup>
$Ca^{2+}_{aq} + 2L_{org} + 2H^+_{org} \rightleftharpoons CaL^{2+}_{2,org} + 2H^+_{aq}$	22.19
$Ca^{2+}_{aq} + 3L_{org} + 2H^+_{org} \rightleftharpoons CaL^{2+}_{3,org} + 2H^+_{aq}$	26.56
$Ca^{2+}_{org} + 2L_{org} \rightleftharpoons CaL^{2+}_{2,org}$	21.99
$Ca^{2+}_{org} + 3L_{org} \rightleftharpoons CaL^{2+}_{3,org}$	26.36

<sup>a</sup> Ref. 35. <sup>b</sup> Ref. 42.

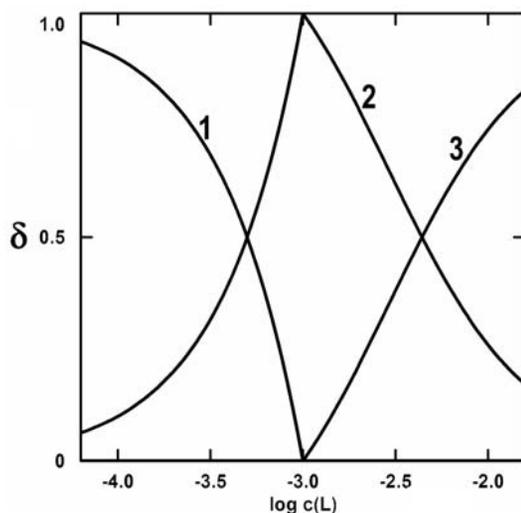
**Table 4.** Equilibrium constants in the water – HCl – Sr<sup>2+</sup> (microamounts) – nitrobenzene – DPPPDO – H<sup>+</sup>B<sup>-</sup> system.

Equilibrium	log K
$L_{aq} \rightleftharpoons L_{org}$	2.38 <sup>a</sup>
$H^+_{org} + L_{org} \rightleftharpoons HL^+_{org}$	9.45 <sup>a</sup>
$H^+_{org} + 2L_{org} \rightleftharpoons HL^+_{2,org}$	11.99 <sup>a</sup>
$Sr^{2+}_{aq} + 2H^+_{org} \rightleftharpoons Sr^{2+}_{org} + 2H^+_{aq}$	0.7 <sup>b</sup>
$Sr^{2+}_{aq} + 2L_{org} + 2H^+_{org} \rightleftharpoons SrL^{2+}_{2,org} + 2H^+_{aq}$	22.21
$Sr^{2+}_{aq} + 3L_{org} + 2H^+_{org} \rightleftharpoons SrL^{2+}_{3,org} + 2H^+_{aq}$	26.23
$Sr^{2+}_{aq} + 4L_{org} + 2H^+_{org} \rightleftharpoons SrL^{2+}_{4,org} + 2H^+_{aq}$	28.48
$Sr^{2+}_{org} + 2L_{org} \rightleftharpoons SrL^{2+}_{2,org}$	21.51
$Sr^{2+}_{org} + 3L_{org} \rightleftharpoons SrL^{2+}_{3,org}$	25.53
$Sr^{2+}_{org} + 4L_{org} \rightleftharpoons SrL^{2+}_{4,org}$	27.78

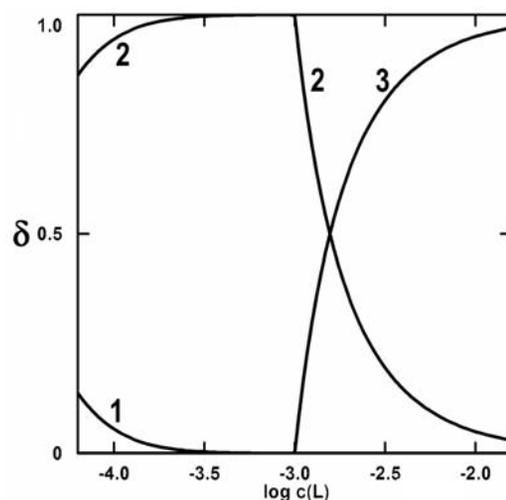
<sup>a</sup> Ref. 35. <sup>b</sup> Ref. 39.

Moreover, Figure 3 depicts the contributions of the species H<sup>+</sup>, HL<sup>+</sup><sub>org</sub> and HL<sup>+</sup><sub>2,org</sub> to the total hydrogen cation concentration in the equilibrium nitrobenzene phase, whereas Figures 4 and 5 show the contributions of the cations Ca<sup>2+</sup>, CaL<sup>2+</sup><sub>2,org</sub>, CaL<sup>2+</sup><sub>3,org</sub> and Sr<sup>2+</sup>, SrL<sup>2+</sup><sub>2,org</sub>, SrL<sup>2+</sup><sub>3,org</sub>, SrL<sup>2+</sup><sub>4,org</sub>, respectively, to the total divalent metal cation concentration in the corresponding equilibrium organic phase. From Figures 3, 4 and 5 it follows that the cationic complex species HL<sup>+</sup><sub>2,org</sub>, CaL<sup>2+</sup><sub>3,org</sub> and SrL<sup>2+</sup><sub>4,org</sub> are present in significant concentrations only at relatively high amounts of the DPPPDO ligand in the systems under consideration.

At this point it should be noted that the stability constants of the calcium and strontium complex species involving the DPPPDO ligand in nitrobenzene saturated with water are  $\log \beta(CaL^{2+}_{2,org}) = 21.99$ ,  $\log \beta(SrL^{2+}_{2,org}) = 21.51$ ,  $\log \beta(CaL^{2+}_{3,org}) = 26.36$  and  $\log \beta(SrL^{2+}_{3,org}) = 25.53$ , as given in Tables 3 and 4. Thus, in the considered nitrobenzene medium, the stability constants of the CaL<sup>2+</sup><sub>n</sub> complexes, where n = 2, 3 and L is DPPPDO, are somewhat higher than those of the corresponding complexes SrL<sup>2+</sup><sub>n</sub>.

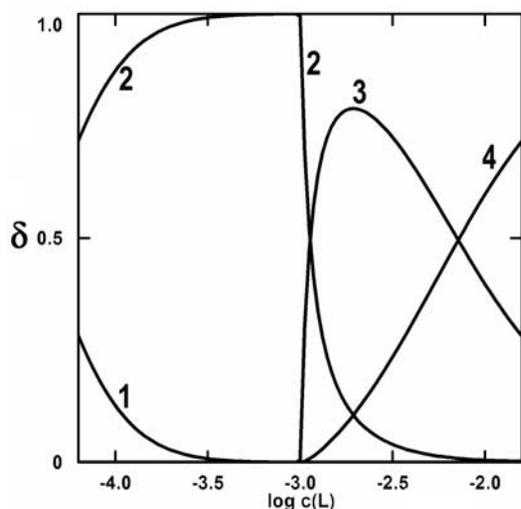


**Figure 3.** Distribution diagram of hydrogen cation in the equilibrium nitrobenzene phase of the water–HCl–Ca<sup>2+</sup>(microamounts)–nitrobenzene–DPPPDO–H<sup>+</sup>B<sup>-</sup> extraction system in the forms of H<sup>+</sup>, HL<sup>+</sup> and HL<sup>+</sup><sub>2</sub>; c(HCl) = 0.01 mol/L, c<sub>B</sub> = 0.001 mol/L.  
 1  $\delta(H^+) = [H^+_{org}]/c(H^+)_{org}$ ,  
 2  $\delta(HL^+) = [HL^+_{org}]/c(H^+)_{org}$ ,  
 3  $\delta(HL^+_2) = [HL^+_{2,org}]/c(H^+)_{org}$ ,  
 where  $c(H^+)_{org} = [H^+_{org}] + [HL^+_{org}] + [HL^+_{2,org}]$ .  
 The distribution curves were calculated using the constants given in Table 3.



**Figure 4.** Distribution diagram of calcium in the equilibrium nitrobenzene phase of the water–HCl–Ca<sup>2+</sup> (microamounts) – nitrobenzene – DPPPDO – H<sup>+</sup>B<sup>-</sup> extraction system in the forms of Ca<sup>2+</sup>, CaL<sup>2+</sup><sub>2</sub> and CaL<sup>2+</sup><sub>3</sub>; c(HCl) = 0.01 mol/L, c<sub>B</sub> = 0.001 mol/L.  
 1  $\delta(Ca^{2+}) = [Ca^{2+}_{org}]/c(Ca^{2+})_{org}$ ,  
 2  $\delta(CaL^{2+}_2) = [CaL^{2+}_{2,org}]/c(Ca^{2+})_{org}$ ,  
 3  $\delta(CaL^{2+}_3) = [CaL^{2+}_{3,org}]/c(Ca^{2+})_{org}$ ,  
 where  $c(Ca^{2+})_{org} = [Ca^{2+}_{org}] + [CaL^{2+}_{2,org}] + [CaL^{2+}_{3,org}]$ .  
 The distribution curves were calculated using the constants given in Table 3.

Finally, it is necessary to emphasize that the stability constants of the complexes CaL<sup>2+</sup><sub>3</sub>, SrL<sup>2+</sup><sub>3</sub> and EuL<sup>3+</sup><sub>3</sub>, with the DPPPDO ligand in water-saturated nitrobenzene are



**Figure 5.** Distribution diagram of strontium in the equilibrium nitrobenzene phase of the water– HCl–Sr<sup>2+</sup> (microamounts) –nitrobenzene– DPPPDO – H<sup>+</sup>B<sup>-</sup> extraction system in the forms of Sr<sup>2+</sup>, SrL<sub>2</sub><sup>2+</sup>, SrL<sub>3</sub><sup>2+</sup> and SrL<sub>4</sub><sup>2+</sup>; c(HCl) = 0.01 mol/L, c<sub>B</sub> = 0.001 mol/L.

$$1 \delta(\text{Sr}^{2+}) = [\text{Sr}_{\text{org}}^{2+}] / c(\text{Sr}^{2+})_{\text{org}}$$

$$2 \delta(\text{SrL}_2^{2+}) = [\text{SrL}_{2,\text{org}}^{2+}] / c(\text{Sr}^{2+})_{\text{org}}$$

$$3 \delta(\text{SrL}_3^{2+}) = [\text{SrL}_{3,\text{org}}^{2+}] / c(\text{Sr}^{2+})_{\text{org}}$$

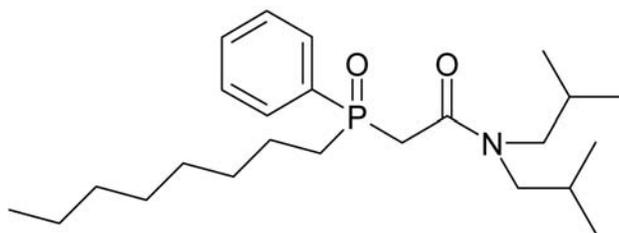
$$4 \delta(\text{SrL}_4^{2+}) = [\text{SrL}_{4,\text{org}}^{2+}] / c(\text{Sr}^{2+})_{\text{org}}$$

$$\text{where } c(\text{Sr}^{2+})_{\text{org}} = [\text{Sr}_{\text{org}}^{2+}] + [\text{SrL}_{2,\text{org}}^{2+}] + [\text{SrL}_{3,\text{org}}^{2+}] + [\text{SrL}_{4,\text{org}}^{2+}].$$

The distribution curves were calculated using the constants given in Table 4.

$\log \beta(\text{CaL}_{3,\text{org}}^{2+}) = 26.36$  (Table 3),  $\log \beta(\text{SrL}_{3,\text{org}}^{2+}) = 25.53$  (Table 4) and  $\log \beta(\text{EuL}_3^{3+}) = 35.80$ .<sup>35</sup> This means that the stability of these three complexes in the mentioned medium increases in the series of Sr<sup>2+</sup> < Ca<sup>2+</sup> << Eu<sup>3+</sup>.

In conclusion, Table 5 summarizes the stability constants of the species HL<sup>+</sup>, HL<sub>2</sub><sup>+</sup>, CaL<sub>2</sub><sup>2+</sup>, CaL<sub>3</sub><sup>2+</sup>, SrL<sub>2</sub><sup>2+</sup>, SrL<sub>3</sub><sup>2+</sup> and SrL<sub>4</sub><sup>2+</sup> with two electroneutral ligands L, denoted by the symbols “classical” CMPO and DPPPDO (see Schemes 1 and 2), in nitrobenzene saturated with water. From the data reviewed in this table it follows that in the considered nitrobenzene medium, the stability constants of the cationic complexes HL<sup>+</sup>, HL<sub>2</sub><sup>+</sup>, CaL<sub>2</sub><sup>2+</sup>, CaL<sub>3</sub><sup>2+</sup>, SrL<sub>2</sub><sup>2+</sup>, SrL<sub>3</sub><sup>2+</sup> and SrL<sub>4</sub><sup>2+</sup> where L = DPPPDO, are substantially higher than those of the corresponding complex species involving the “classical” CMPO ligand.



**Scheme 2.** Structural formula of octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (abbrev. “classical” CMPO).

**Table 5.** Stability constants of the complex species HL<sup>+</sup>, HL<sub>2</sub><sup>+</sup>, CaL<sub>2</sub><sup>2+</sup>, CaL<sub>3</sub><sup>2+</sup>, SrL<sub>2</sub><sup>2+</sup>, SrL<sub>3</sub><sup>2+</sup> and SrL<sub>4</sub><sup>2+</sup> [L = octyl-phenyl-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (“classical” CMPO), 2,6-(diphenylphosphino)pyridine dioxide (DPPPDO)] in nitrobenzene saturated with water at 25 °C.

Quantity	L	
	“classical” CMPO <sup>a</sup>	DPPPDO <sup>b</sup>
$\log \beta(\text{HL}_{\text{org}}^+)$	6.16	9.45 <sup>c</sup>
$\log \beta(\text{HL}_{2,\text{org}}^+)$	9.29	11.99 <sup>c</sup>
$\log \beta(\text{CaL}_{2,\text{org}}^{2+})$	14.46	21.99
$\log \beta(\text{CaL}_{3,\text{org}}^{2+})$	19.52	26.36
$\log \beta(\text{SrL}_{2,\text{org}}^{2+})$	13.09	21.51
$\log \beta(\text{SrL}_{3,\text{org}}^{2+})$	17.31	25.53
$\log \beta(\text{SrL}_{4,\text{org}}^{2+})$	18.96	27.78

<sup>a</sup> Ref. 14. <sup>b</sup> This work. <sup>c</sup> Ref. 35.

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## 5. References

1. E. Makrlík, P. Vaňura, *Talanta* **1985**, 32, 423–429.
2. E. Makrlík, P. Vaňura, P. Selucký, *J. Solution Chem.* **2009**, 38, 1129–1138.
3. E. Makrlík, P. Vaňura, P. Selucký, *J. Solution Chem.* **2010**, 39, 692–700.
4. E. Makrlík, J. Budka, P. Vaňura, *Acta Chim. Slov.* **2009**, 56, 278–281.
5. E. Makrlík, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smirnov, *Acta Chim. Slov.* **2009**, 56, 718–722.
6. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2009**, 56, 475–479.
7. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2009**, 56, 973–976.
8. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 470–474.
9. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 485–490.
10. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2010**, 57, 922–926.
11. E. Makrlík, P. Toman, P. Vaňura, R. Rathore, *Acta Chim. Slov.* **2010**, 57, 948–952.
12. E. Makrlík, P. Vaňura, P. Selucký, *Acta Chim. Slov.* **2011**, 58, 176–180.
13. E. Makrlík, P. Vaňura, *Z. Phys. Chem.* **2009**, 223, 247–252.
14. E. Makrlík, P. Vaňura, P. Selucký, *Z. Phys. Chem.* **2009**, 223, 253–261.
15. E. Makrlík, J. Dybal, P. Vaňura, *Z. Phys. Chem.* **2009**, 223, 713–718.

16. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2009**, 279, 137–142.
17. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2009**, 279, 287–291.
18. E. Makrlík, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smirnov, *J. Radioanal. Nucl. Chem.* **2009**, 279, 743–747.
19. E. Makrlík, P. Vaňura, Z. Sedláková, *J. Radioanal. Nucl. Chem.* **2009**, 280, 607–611.
20. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2009**, 281, 547–551.
21. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2009**, 281, 633–638.
22. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 283, 45–50.
23. E. Makrlík, P. Vaňura, Z. Sedláková, *J. Radioanal. Nucl. Chem.* **2010**, 283, 157–161.
24. E. Makrlík, P. Vaňura, *J. Radioanal. Nucl. Chem.* **2010**, 283, 497–501.
25. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 283, 571–575.
26. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 283, 727–733.
27. E. Makrlík, P. Vaňura, P. Selucký, V. A. Babain, I. V. Smirnov, *J. Radioanal. Nucl. Chem.* **2010**, 283, 839–844.
28. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 284, 87–92.
29. E. Makrlík, P. Vaňura, P. Selucký, *J. Radioanal. Nucl. Chem.* **2010**, 285, 383–387.
30. V. N. Romanovskiy, I. V. Smirnov, V. A. Babain, T. A. Todd, R. S. Herbst, J. D. Law, K. N. Brewer, *Solvent Extr. Ion Exch.* **2001**, 19, 1–21.
31. J. D. Law, R. S. Herbst, T. A. Todd, V. N. Romanovskiy, V. A. Babain, V. M. Esimantovskiy, I. V. Smirnov, B. N. Zaitsev, *Solvent Extr. Ion Exch.* **2001**, 19, 23–36.
32. W. W. Schulz, E. P. Horwitz, *Separ. Sci. Technol.* **1988**, 23, 1191–1210.
33. C. Cuillardier, C. Musikas, P. Hoel, L. Nigond, X. Vitart, *Separ. Sci. Technol.* **1991**, 26, 1229–1244.
34. G. R. Mahajan, D. R. Prabhu, V. K. Manchanda, L. P. Badheka, *Waste Management* **1998**, 18, 125–133.
35. E. Makrlík, P. Vaňura, P. Selucký, Z. Spíchal, *Acta Chim. Slov.* **2011**, 58, 600–604.
36. R. Ševčík, M. Nečas, J. Novosad, *Polyhedron* **2003**, 22, 1585–1593.
37. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, 90, 879–896.
38. E. Makrlík, *Collect. Czech. Chem. Commun.* **1992**, 57, 289–295.
39. P. Vaňura, E. Makrlík, J. Rais, M. Kyrš, *Collect. Czech. Chem. Commun.* **1982**, 47, 1444–1464.
40. P. Vaňura, E. Makrlík, *Collect. Czech. Chem. Commun.* **1993**, 58, 1324–1336.
41. L. G. Sillén, B. Warnqvist, *Arkiv Kemi* **1996**, 31, 315–339.
42. P. Vaňura, *Czech. J. Phys.* **1999**, 49 (Suppl. S1), 761–767.

## Povzetek

Proučevali smo ekstrakcijo mikrokoličin kalcija in stroncija z raztopino hidrogen dikarbolilkobaltata ( $H^+B^-$ ) v prisotnosti 2,6-(difenilfosfino)piridin dioksida (DPPPDO, L). Eksperimentalne podatke smo analizirali ob predpostavki, da se kompleksi  $HL^+$ ,  $HL_2^+$ ,  $CaL_2^{2+}$ ,  $CaL_3^{2+}$ ,  $SrL_2^{2+}$ ,  $SrL_3^{2+}$  in  $SrL_4^{2+}$  ekstrahirajo v organsko fazo. Določili smo koeficiente porazdelitve in konstante stabilnosti kompleksov v nitrobenzenu, nasičenem z vodo.