

## EXTRACTION OF $^{133}\text{Ba}$ WITH BIS[UNDECAHYDRO-7,8-DICARBA-UNDECABORATO(2-)]COBALTATE(1-) IN THE PRESENCE OF DIBENZO-18-CROWN-6

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Extraction of barium with the nitrobenzene solution of bis[undecahydro-7,8-dicarbaundecaborato(2-)]cobaltate(1-) in the presence of dibenzo-18-crown-6 (DB18C6, L) has been investigated. The equilibrium data and typical maxima in the dependences of the Ba distribution ratios on the analytical concentration of DB18C6 in the system can be explained assuming that the species  $\text{Ba}^{2+}$ ,  $\text{BaL}^{2+}$ ,  $\text{BaL}_2^{2+}$ ,  $\text{BaHL}^{3+}$  and  $\text{BaHL}_2^{3+}$  to be extracted into the nitrobenzene phase. The values of extraction and stability constants of the species in nitrobenzene saturated with water have been determined.

**Key words:** Water–nitrobenzene extraction system; Barium; Crown ethers; Dibenzo-18-crown-6; Carboranes; Bis-1,2-dicarbollylcobaltate.

In our previous works<sup>1-4</sup>, we dealt with the extraction of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  ions using a nitrobenzene solution of  $\text{H}^+ - \text{bis}[\text{undecahydro-7,8-dicarbaundecaborato(2-)]\text{cobaltate(1-)}$  (bis-1,2-dicarbollylcobaltate,  $\text{H}^+\text{B}^-$ ) in the presence of polyethylene glycols, polyethers and crowns. These ions ( $\text{M}^{2+}$ ) have been found to be extracted in the form of the  $\text{ML}_{n,\text{org}}^{2+}$  complexes. The occurrence of maxima on the plot of metal ion distribution ratio  $D$  vs the total polyether concentration  $c(\text{L})$  has been explained in terms of competition between the charged  $\text{ML}_{n,\text{org}}^{2+}$  complexes and protonated PEG ( $\text{HL}_{\text{org}}^+$ ) in the balancing of the dicarbollylcobaltate electrostatic charge in the organic phase.

Quite different behaviour has been found in the extraction of perchloric acid with nitrobenzene solution of dibenzo-18-crown-6 compared with the extraction of the acid into nitrobenzene in the presence of 18-crown-6 (refs<sup>5,6</sup>). Extraction of cesium using a nitrobenzene solution of  $\text{H}^+\text{B}^-$  in the presence of dibenzo-18-crown-6 has been investigated<sup>7</sup>.

The aim of this paper is to study the extraction of barium with the nitrobenzene solution of  $\text{H}^+\text{B}^-$  in the presence of dibenzo-18-crown-6 (DB18C6). We intended to find the composition of species in the organic phase and to determine the respective equilibrium constants.

## EXPERIMENTAL

Dibenzo-18-crown-6 (98%, Fluka, Buchs, Switzerland) was used without additional purification. Cesium salt of bis-1,2-dicarbolylcobaltate,  $\text{Cs}^+\text{B}^-$ , was synthesized in the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Rez near Prague. Hydrogen form of bis-1,2-dicarbolylcobaltate ( $\text{H}^+\text{B}^-$ ) was prepared from the corresponding cesium salt ( $\text{Cs}^+\text{B}^-$ ) by the procedure described in ref.<sup>3</sup>. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide  $^{133}\text{Ba}$  was of standard radiochemical purity.

The extraction experiments in a two-phase water– $\text{HClO}_4$ – $\text{Ba}^{2+}$  (microamounts)–nitrobenzene– $\text{H}^+\text{B}^-$ –DB18C6 system were performed in 10 ml glass test-tubes with polyethylene stoppers using 2 ml of each phase. The test-tubes were shaken for one hour at  $25 \pm 2$  °C using a laboratory shaker. Under these conditions the equilibrium in the system under study has been established already after approximately 20 min shaking. Then the phases were separated by centrifugation (5 min, 2 500 rpm). After centrifugation, 1 ml samples were taken from each phase and their  $\gamma$  activities were measured using a well-type NaI(Tl) scintillation detector in connection with a single-channel  $\gamma$  analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of barium,  $D$ , was determined as a ratio of the measured activities of the nitrobenzene and aqueous samples.

## RESULTS AND DISCUSSION

For the system under study, the dependences of the logarithm of the barium distribution ratios ( $\log D$ ) on the logarithm of the total (analytical) concentration of the crown in the system ( $\log c(\text{L})$ ) were experimentally measured for various concentration of perchloric acid in the aqueous phase ( $c(\text{HClO}_4) = 0.05\text{--}0.20$  mol  $\text{l}^{-1}$ ) and for various concentrations of bis-1,2-dicarbolylcobaltate in the nitrobenzene phase ( $c(\text{B}) = 0.0025\text{--}0.025$  mol  $\text{l}^{-1}$ ) in the presence of DB18C6 ( $c(\text{L}) = 9 \cdot 10^{-6}\text{--}1 \cdot 10^{-2}$  mol  $\text{l}^{-1}$ ). The corresponding results are given in Fig. 1 and Table I.

It is necessary to emphasize that the distribution ratios of barium decrease with the second power of acidity of the aqueous phase, but the dependence of  $D$  on the concen-

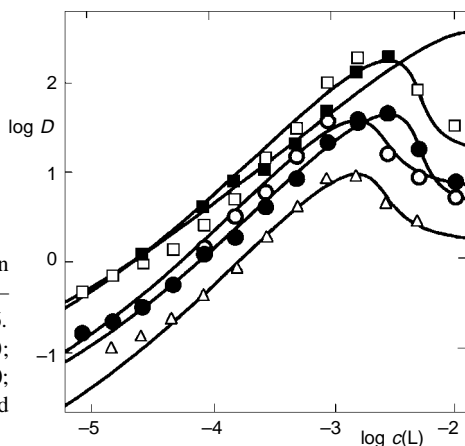


FIG. 1

Logarithms  $D$  as a function of logarithms  $c(\text{L})$  in the system water– $\text{HClO}_4$ – $\text{Ba}^{2+}$  (microamounts)–nitrobenzene–bis-1,2-dicarbolylcobaltate–DB18C6.  $c(\text{B})$ ,  $c(\text{HClO}_4)$ , mol  $\text{l}^{-1}$ :  $\circ$  0.0025, 0.050;  $\square$  0.0050, 0.050;  $\triangle$  0.0025, 0.10;  $\bullet$  0.0050, 0.10;  $\blacksquare$  0.025, 0.20. The solid curves were calculated for the constants given in Table III

tration of dicarbollylcobaltate in the nitrobenzene phase is very complicated and hence the experimental data cannot be described using a simple assumption that only the  $\text{BaL}_{n,\text{org}}^{2+}$  ( $n = 0-2$ ) species exist in the organic phase. Since the extracted metal is present in trace concentrations, no dimerization of crown-metal complexes can be expected. On the other hand, the extraction of the protonated particles  $\text{BaH}_p\text{L}_{s,\text{org}}^{(r+2)+}$  is quite possible.

With regard to the results of previous papers<sup>1-5</sup>, the two-phase water- $\text{HClO}_4$ - $\text{Ba}^{2+}$  (microamounts)-nitrobenzene- $\text{H}^+\text{B}^-$ -DB18C6 system can be described by the set of reactions

$$L_{\text{aq}} = L_{\text{org}} \quad (\text{A})$$

$$p \text{H}_{\text{org}}^+ + q L_{\text{org}} = \text{H}_p\text{L}_{q,\text{org}}^{p+} \quad (\text{B})$$

TABLE I

Logarithm of distribution ratio  $D$  as a function of  $\log c(\text{L})$  ( $\text{L} = \text{DB18C6}$ ) for barium extraction from the aqueous solution of perchloric acid with the nitrobenzene solution of bis-1,2-dicarbollylcobaltate

$$c(\text{HClO}_4) = 0.05 \text{ mol l}^{-1}, c(\text{B}) = 0.0025 \text{ mol l}^{-1}$$

-4.046 0.152; -3.796 0.499; -3.553 0.769; -3.301 1.169; -3.046 1.565; 2.796 1.543;  
-2.553 1.193; -2.301 0.929; -2.000 0.702

$$c(\text{HClO}_4) = 0.05 \text{ mol l}^{-1}, c(\text{B}) = 0.0050 \text{ mol l}^{-1}$$

-5.046 -0.348; -4.796 -0.162; -4.533 0.006; -4.301 0.121; -4.046 0.392; -3.796 0.699;  
-3.553 1.129; -3.301 1.494; -3.046 1.984; -2.796 2.252; -2.553 2.299; -2.301 1.891;  
-2.000 1.482

$$c(\text{HClO}_4) = 0.10 \text{ mol l}^{-1}, c(\text{B}) = 0.0025 \text{ mol l}^{-1}$$

-4.796 -0.963; -4.553 -0.838; -4.301 -0.639; -4.046 -0.374; -3.796 -0.050; -3.553 0.294;  
-3.301 0.630; -3.046 0.919; -2.796 0.948; -2.553 0.632; -2.301 0.415

$$c(\text{HClO}_4) = 0.10 \text{ mol l}^{-1}, c(\text{B}) = 0.0050 \text{ mol l}^{-1}$$

-5.046 -0.802; -4.796 -0.671; -4.553 -0.514; -4.301 -0.262; -4.046 0.079; -3.796 0.266;  
-3.553 0.601; -3.301 0.917; -3.046 1.322; -2.796 1.577; -2.553 1.645; -2.301 1.246;  
-2.000 0.877

$$c(\text{HClO}_4) = 0.20 \text{ mol l}^{-1}, c(\text{B}) = 0.025 \text{ mol l}^{-1}$$

-4.553 0.065; -4.046 0.591; -3.796 0.883; -3.553 1.045; -3.301 1.299; -3.046 1.669;  
-2.796 2.102; -2.553 2.303



to which the following equilibrium constants

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

$$K(\text{H}_p\text{L}_{q,\text{org}}^{p+}) = \frac{[\text{H}_p\text{L}_{q,\text{org}}^{p+}]}{[\text{H}_{\text{org}}^{+}]^p [\text{L}_{\text{org}}]^q} \quad (\text{2})$$

$$K_{\text{ex}}(\text{BaH}_r\text{L}_{s,\text{org}}^{(r+2)+}) = \frac{[\text{BaH}_r\text{L}_{s,\text{org}}^{(r+2)+}] [\text{H}_{\text{aq}}^{+}]^2}{[\text{Ba}_{\text{aq}}^{2+}] [\text{H}_{\text{org}}^{+}]^{(r+2)} [\text{L}_{\text{org}}]^s} \quad (\text{3})$$

$$K(\text{BaL}_{\text{aq}}^{2+}) = \frac{[\text{BaL}_{\text{aq}}^{2+}]}{[\text{Ba}_{\text{aq}}^{2+}] [\text{L}_{\text{aq}}]} \quad (\text{4})$$

correspond.

A subroutine UBBE, based on the relations given above, mass balances of the crown ligand and the electroneutrality conditions of both phases, was formulated<sup>1,4</sup> and introduced into the more general least-squares minimizing program LETAGROP (ref.<sup>8</sup>) which was used for the evaluation of the “best” values of the constants  $K_{\text{ex}}(\text{BaH}_r\text{L}_{s,\text{org}}^{(r+2)+})$ . The minimum the error square sum of  $\log D$ , *i.e.* the minimum of the expression

$$U = \sum (\log D_{\text{calc}} - \log D_{\text{exp}})^2 \quad (\text{5})$$

was sought.

The following values were used for the respective calculations:  $\log K(\text{HL}_{\text{org}}^{+}) = 3.83$  (ref.<sup>6</sup>),  $\log K(\text{H}_2\text{L}_{2,\text{org}}^{2+}) = 10.43$  (ref.<sup>6</sup>),  $\log K_{\text{ex}}(\text{Ba}^{2+}) = 0.85$  (ref.<sup>2</sup>),  $\log K_D = 4.36$  (ref.<sup>9</sup>) and  $\log K(\text{BaL}_{\text{aq}}^{2+}) = 1.95$  (ref.<sup>10</sup>). The results are presented in Table II.

From Table II it is evident that the assumption of the extraction of the species  $\text{Ba}^{2+}$ ,  $\text{BaL}_{\text{aq}}^{2+}$  and  $\text{BaL}_{2,\text{aq}}^{2+}$ , which is appropriate for the description of the extraction of strontium and barium in the presence of 18-crown-6 (ref.<sup>4</sup>), is not satisfactory in the case of the

system under study. On the other hand, considering the existence of the protonated complexes  $\text{BaHL}^{3+}$  and  $\text{BaHL}_2^{3+}$  (analogously to the complex  $\text{H}_2\text{L}_2^{2+}$ , ref.<sup>6</sup>), the agreement between the theoretical and experimental values becomes substantially better. Similar results have been found for the reactions of  $\text{Na}^+$  ion with a few crowns (15-crown-5, benzo-15-crown-5, 18-crown-6 and benzo-18-crown-6) in water<sup>11</sup>.

TABLE II

Comparison of various models of barium extraction from aqueous solution of perchloric acid with nitrobenzene solutions of bis-1,2-dicarbollycobaltate in the presence of dibenzo-18-crown-6

Model	$\log K_{\text{ex}}^a$	$U^b$
$\text{Ba}^{2+}, \text{BaL}^{2+}$	0.85, $8.68 \pm 0.20$	11.791721
$\text{Ba}^{2+}, \text{BaHL}_2^{3+}$	0.85, $15.31 \pm 0.13$	32.460035
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaHL}^{3+}$	0.85, $8.67 \pm 0.25$ , 9.23(10.46)	11.781554
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}$	0.85, $8.49 \pm 0.17$ , 12.14(12.43)	5.477795
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaHL}_2^{3+}$	0.85, $8.03 \pm 0.22$ , $15.91 \pm 0.13$	2.109519
$\text{Ba}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}$	0.85, 11.77(11.97), $10.36 \pm 0.13$ , $15.79 \pm 0.10$	0.833363
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}$	0.85, 7.70(7.97), $11.77 \pm 0.24$ , $10.16 \pm 0.24$ , $15.77 \pm 0.10$	0.665687
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}, \text{BaH}_{-1}\text{L}_2^+$	transforms to $\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}$	
$\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}, \text{BaH}_{-1}\text{L}^+, \text{BaH}_{-1}\text{L}_2^+$	transforms to $\text{Ba}^{2+}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}$	
$\text{Ba}^{2+,c}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}$	1.53(1.82), 7.46(7.87), $11.75 \pm 0.23$ , 10.06(10.28), $15.81 \pm 0.10$	0.578147
$\text{Ba}^{2+,c}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}, \text{BaH}_{-1}\text{L}^+$	1.53(1.83), 7.37(8.09), 11.70(12.21), 10.07(10.31), $15.8 \pm 0.11$ , 4.08(5.35)	0.577777
$\text{Ba}^{2+,c}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}, \text{BaH}_{-1}\text{L}^+, \text{BaH}_{-1}\text{L}_2^+$	transforms to $\text{Ba}^{2+,c}, \text{BaL}^{2+}, \text{BaL}_2^{2+}, \text{BaHL}^{3+}, \text{BaHL}_2^{3+}, \text{BaH}_{-1}\text{L}^+$	

<sup>a</sup> The values of extraction constants are given for each complex. The following values were used for the computations:  $\log K_D = 4.36$  (ref.<sup>9</sup>),  $\log K(\text{HL}_{\text{org}}^+) = 3.83$  (ref.<sup>6</sup>),  $\log K(\text{H}_2\text{L}_{2,\text{org}}^{2+}) = 10.43$  (ref.<sup>6</sup>),  $\log K_{\text{ex}}(\text{Ba}^{2+}) = 0.85$  (ref.<sup>2</sup>) and  $\log K(\text{BaL}_{\text{aq}}^{2+}) = 1.95$  (ref.<sup>10</sup>). The reliability interval of the constants is given – in agreement with ref.<sup>8</sup> – as  $3s(K)$ , where  $s(K)$  is the standard deviation of the constant  $K$ . These values are expressed in the logarithmic scale using the approximate relation  $\log K \pm \{[\log(K + 1.5s(K))] - [\log(K - 1.5s(K))]\}$ . For  $s(K) > 0.2K$ , the previous relation is not valid and then only the upper limit is given in the parenthesis in the form  $\log K\{\log[K + 3s(K)]\}$ . <sup>b</sup> The error-square sum  $U = \Sigma(\log D_{\text{calc}} - \log D_{\text{exp}})^2$ . <sup>c</sup> The exchange extraction constant  $K_{\text{ex}}(\text{Ba}^{2+})$  was also minimized.

Figure 2 presents the contribution of the species  $\text{H}^+_{\text{org}}$ ,  $\text{HL}^+_{\text{org}}$  and  $\text{H}_2\text{L}^{2+}_{\text{org}}$  to the total acidity of the organic phase while Fig. 3 depicts the contribution of the species  $\text{Ba}^{2+}_{\text{org}}$ ,  $\text{BaL}^{2+}_{\text{org}}$ ,  $\text{BaL}^{2+}_{2,\text{org}}$ ,  $\text{BaHL}^{3+}_{\text{org}}$  and  $\text{BaHL}^{3+}_{2,\text{org}}$  to the total barium concentration in the organic phase.

Knowing the value  $\log K_{\text{ex}}(\text{Ba}^{2+}) = 0.85$  (ref.<sup>2</sup>) and the extraction constants  $\log K_{\text{ex}}(\text{BaL}^{2+}_{\text{org}}) = 7.70$  and  $\log K_{\text{ex}}(\text{BaL}^{2+}_{2,\text{org}}) = 11.77$ , determined in this paper, the stability constants of the complexes  $\text{BaL}^{2+}$  and  $\text{BaL}^{2+}_2$  in the nitrobenzene phase defined as

$$K(\text{BaL}^{2+}_{\text{org}}) = \frac{[\text{BaL}^{2+}_{\text{org}}]}{[\text{Ba}^{2+}_{\text{org}}][\text{L}_{\text{org}}]} \quad (6)$$

$$\beta(\text{BaL}^{2+}_{2,\text{org}}) = \frac{[\text{BaL}^{2+}_{2,\text{org}}]}{[\text{Ba}^{2+}_{\text{org}}][\text{L}_{\text{org}}]^2} \quad (7)$$

can be evaluated on the basis of the simple relations:

$$\log K(\text{BaL}^{2+}_{\text{org}}) = \log K_{\text{ex}}(\text{BaL}^{2+}_{\text{org}}) - \log K_{\text{ex}}(\text{Ba}^{2+}) \quad (8)$$

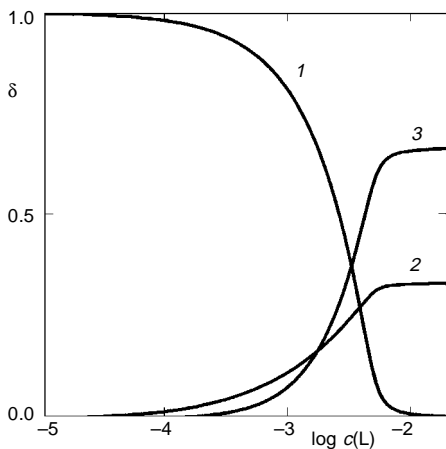


FIG. 2

The dependence of the fraction of the protonated species ( $\delta$ ) present in the organic phase of the system water– $\text{HClO}_4$ – $\text{Ba}^{2+}$  (microamounts)–nitrobenzene–bis-1,2-dicarbolylcobaltate–DB18C6 on  $\log c(\text{L})$ .  $c(\text{B}) = 0.0050 \text{ mol l}^{-1}$ ,  $c(\text{HClO}_4) = 0.10 \text{ mol l}^{-1}$ .  $\delta$  values for: 1  $\text{H}^+$ , 2  $\text{HL}^+$ , 3  $\text{H}_2\text{L}^{2+}$ . The solid curves were calculated for the constants  $\log K_D = 4.36$ ,  $\log K(\text{HL}^+_{\text{org}}) = 3.83$  and  $\log K(\text{H}_2\text{L}^{2+}_{\text{org}}) = 10.43$

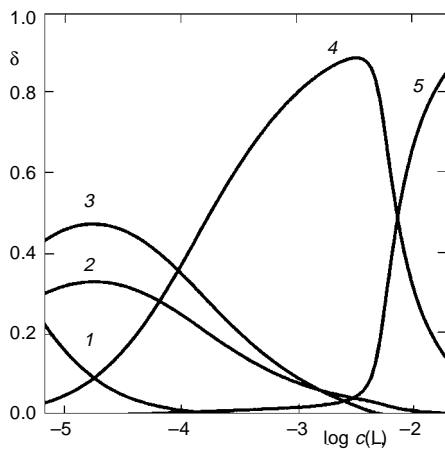
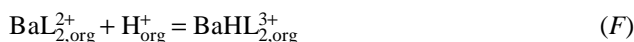


FIG. 3

The dependence of the fraction of the Ba-containing species ( $\delta$ ) present in the organic phase of the system water– $\text{HClO}_4$ – $\text{Ba}^{2+}$  (microamounts)–nitrobenzene–bis-1,2-dicarbolylcobaltate–DB18C6 on  $\log c(\text{L})$ .  $c(\text{B}) = 0.0050 \text{ mol l}^{-1}$ ,  $c(\text{HClO}_4) = 0.10 \text{ mol l}^{-1}$ .  $\delta$  values for: 1  $\text{Ba}^{2+}$ , 2  $\text{BaL}^{2+}$ , 3  $\text{BaHL}^{3+}$ , 4  $\text{BaHL}^{3+}_2$ , 5  $\text{BaL}^{2+}_2$ . The solid curves were calculated for the constants given in Table III

$$\log \beta(\text{BaL}_{2,\text{org}}^{2+}) = \log K_{\text{ex}}(\text{BaL}_{2,\text{org}}^{2+}) - \log K_{\text{ex}}(\text{Ba}^{2+}). \quad (9)$$

Similarly, the protonation constants of cations  $\text{BaL}_{\text{org}}^{2+}$  and  $\text{BaL}_{2,\text{org}}^{2+}$  in nitrobenzene saturated with water, *i.e.*, the equilibrium constants of the following reactions



defined as

$$K(\text{BaHL}_{\text{org}}^{3+}) = \frac{[\text{BaHL}_{\text{org}}^{3+}]}{[\text{BaL}_{\text{org}}^{2+}][\text{H}_{\text{org}}^{+}]} \quad (10)$$

$$K(\text{BaHL}_{2,\text{org}}^{3+}) = \frac{[\text{BaHL}_{2,\text{org}}^{3+}]}{[\text{BaL}_{2,\text{org}}^{2+}][\text{H}_{\text{org}}^{+}]} \quad (11)$$

were determined using relations (12) and (13):

$$\log K(\text{BaHL}_{\text{org}}^{3+}) = \log K_{\text{ex}}(\text{BaHL}_{\text{org}}^{3+}) - \log K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+}) \quad (12)$$

$$\log K(\text{BaHL}_{2,\text{org}}^{3+}) = \log K_{\text{ex}}(\text{BaHL}_{2,\text{org}}^{3+}) - \log K_{\text{ex}}(\text{BaL}_{2,\text{org}}^{2+}). \quad (13)$$

Finally, the individual extraction constant of the  $\text{BaL}^{2+}$  cation, denoted  $K_i(\text{BaL}^{2+})$ , in the water–nitrobenzene system and the standard Gibbs energy corresponding to the transfer of that complex cation from the aqueous into the nitrobenzene phase,  $\Delta G_{\text{tr}}^0(\text{BaL}^{2+})$  (ref.<sup>12</sup>), were evaluated using the following equations:

$$\log K_i(\text{BaL}^{2+}) = \log K_{\text{ex}}(\text{BaL}_{\text{org}}^{2+}) - \log K(\text{BaL}_{\text{aq}}^{2+}) + \log K_D + 2 \log K_i(\text{H}^{+}) \quad (14)$$

$$\Delta G_{\text{tr}}^0(\text{BaL}^{2+}) = -2.303 RT \log K_i(\text{BaL}^{2+}) \quad (15)$$

where  $\log K_i(\text{H}^+) = -5.7$  (ref.<sup>12</sup>). The corresponding equilibrium constants are summarized in Table III.

In conclusion it should be noted that similar results were found for the system water– $\text{HClO}_4$ – $\text{Sr}^{2+}$  (microamounts)–nitrobenzene– $\text{H}^+\text{B}^-$ –DB18C6 (ref.<sup>13</sup>). However, the presence of the complex  $\text{SrL}^{2+}$  in the organic phase could not be unambiguously proved by the experimental data because the addition of the complex to the model assuming the extraction of the particles  $\text{Sr}^{2+}$ ,  $\text{SrL}_2^{2+}$ ,  $\text{SrHL}^{3+}$  and  $\text{SrHL}_2^{3+}$  improves the fit of the theoretical and experimental values of  $\log D$  only if the dimerization of the species  $\text{HL}_{\text{org}}^+$  is neglected<sup>13</sup>.

TABLE III  
The equilibrium constants in the water– $\text{HClO}_4$ – $\text{Ba}^{2+}$  (microamounts)–nitrobenzene–bis-1,2-dicarbonylcobaltate–DB18C6 system

Reaction	$\log K$
$\text{L}_{\text{aq}} = \text{L}_{\text{org}}$	4.36 <sup>a</sup>
$\text{H}_{\text{org}}^+ + \text{L}_{\text{org}} = \text{HL}_{\text{org}}^+$	3.83 <sup>b</sup>
$2 \text{H}_{\text{org}}^+ + 2 \text{L}_{\text{org}} = \text{H}_2\text{L}_{2,\text{org}}^{2+}$	10.43 <sup>b</sup>
$\text{Ba}_{\text{aq}}^{2+} + \text{L}_{\text{aq}} = \text{BaL}_{\text{aq}}^{2+}$	1.95 <sup>c</sup>
$\text{Ba}_{\text{aq}}^{2+} + 2 \text{H}_{\text{org}}^+ = \text{Ba}_{\text{org}}^{2+} + 2 \text{H}_{\text{aq}}^+$	0.85 <sup>d</sup>
$\text{Ba}_{\text{aq}}^{2+} + 2 \text{H}_{\text{org}}^+ + \text{L}_{\text{org}} = \text{BaL}_{\text{org}}^{2+} + 2 \text{H}_{\text{aq}}^+$	7.70(7.97)
$\text{Ba}_{\text{aq}}^{2+} + 2 \text{H}_{\text{org}}^+ + 2 \text{L}_{\text{org}} = \text{BaL}_{2,\text{org}}^{2+} + 2 \text{H}_{\text{aq}}^+$	11.77 ± 0.24
$\text{Ba}_{\text{aq}}^{2+} + 3 \text{H}_{\text{org}}^+ + \text{L}_{\text{org}} = \text{BaHL}_{\text{org}}^{3+} + 2 \text{H}_{\text{aq}}^+$	10.16 ± 0.24
$\text{Ba}_{\text{aq}}^{2+} + 3 \text{H}_{\text{org}}^+ + 2 \text{L}_{\text{org}} = \text{BaHL}_{2,\text{org}}^{3+} + 2 \text{H}_{\text{aq}}^+$	15.77 ± 0.10
$\text{Ba}_{\text{org}}^{2+} + \text{L}_{\text{org}} = \text{BaL}_{\text{org}}^{2+}$	6.86
$\text{Ba}_{\text{org}}^{2+} + 2 \text{L}_{\text{org}} = \text{BaL}_{2,\text{org}}^{2+}$	10.93
$\text{BaL}_{\text{org}}^{2+} + \text{H}_{\text{org}}^+ = \text{BaHL}_{\text{org}}^{3+}$	2.46
$\text{BaL}_{2,\text{org}}^{2+} + \text{H}_{\text{org}}^+ = \text{BaHL}_{2,\text{org}}^{3+}$	4.00
$\log K_i(\text{BaL}^{2+})$	-1.3
$\Delta G_{\text{tr}}^0(\text{BaL}^{2+}), \text{kJ mol}^{-1}$	7.4

<sup>a</sup> Ref.<sup>9</sup>; <sup>b</sup> ref.<sup>6</sup>; <sup>c</sup> ref.<sup>10</sup>; <sup>d</sup> ref.<sup>2</sup>.



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