Solvent Extraction of In(III) with 25,26,27,28-Tetrakis[(ethoxycarbonyl)methoxy]-*p-tert-* Butylcalix[4]arene and Crystal Structure of the Extracted Complex *

ZHIXIAN ZHOU[†], LI MA, YANJUN XING, XIAN XIN ZHANG[‡], CHENXIA DU, YALIN SHI and YANGJIE WU
Department of Chemistry, Zhengzhou University, Zhengzhou, 450052, People's Republic of China

Abstract

The extraction of indium(III) with 25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-*p-tert*-butylcalix[4]arene (**L**) into 1,2-dichloroethane was investigated. The presence of Na^+ and Br^- in the aqueous phase was necessary for the extraction. The study showed that the In(III) was extracted by forming an ion-pair compound of $[NaL^+][InBr_4^-]$. The effect of competing ions on the extraction of In(III) was examined. The corresponding extracted complex $[NaL][InBr_4]$ was prepared and characterized by elemental analysis, IR and X-ray structure analysis. The complex crystallized in the monoclinic space group P21/c with $a = 14.504(3)$, $b = 23.270(5)$, $c = 20.290(4)$ Å, $\beta = 93.02(3)°$, $V = 6893(2)$ Å^3, $Z = 4$.

Introduction

It is known that calix[4]arene esters are well pre-organized to complex alkali metal cations, especially sodium ion [1–6]. Indeed, very stable complexes of Na^+ with calix[4]arene esters have been reported [7]. Recently, a novel extraction system was developed to extract perrhenate in the presence of sodium ion with 25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-*p-tert*-butylcalix[4]arene[**L**] [8]. The crystal structural analysis shows that the extracted complex consists of $[NaL]^+$ and ReO_4^-, which suggests that the anion ReO_4^- possessing a certain degree of hydrophobicity can be effectively extracted by ligand **L** which is capable of forming a stable cationic complex with Na^+. The equilibrium may be expressed as follows:

$$Na^+ + L_o + A^- = NaLA_o,$$

where the subscript "o" denotes the organic phase and the lack of it refers to the aqueous phase, and A denotes the anion.

Indium is an industrially important metal and hence its separation and purification are desired. Because In(III) can form the stable anionic complex $InBr_4^-$, the use of hydrophobic macrocyclic compounds to extract In(III) in the presence of NaBr, KBr, KI [9, 10], and high concentrations of acids [11] has been examined. In this paper, we report the extraction of In(III) by calix[4]arene **L** in the presence of NaBr. The results indicate that this extraction system is effective for the separation of micro-amounts of indium from large amounts of cations (Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, Al^{3+} and Fe^{2+}) and anions (NO_3^-, SO_4^{2-}, Cl^-, SCN^-, ClO_4^- and citrate). The extraction mechanism of this novel system has been elucidated by the characterization of the extracted complex obtained by a saturated-extraction method, and X-ray structural analysis of the crystalline complex prepared by recrystallization of the saturated-extraction product.
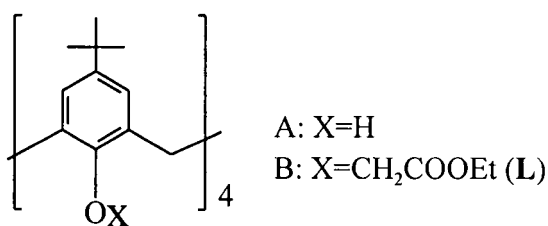
Experimental

Reagents

p-tert-Butylcalix[4]arene (A) and *cone*-25,26,27,28-tetrakis[(ethoxycarbonyl) methoxy]-*p-tert*-butylcalix[4]arene(B) [**L**] (Scheme 1) were synthesized according to literature methods [5, 12]. The standard indium solution was prepared by dissolving 0.1000 g of indium metal (99%) in 5 mL of HCl (1 : 1) and then diluted to 100.0 mL with 0.01 mol dm^{-3} HCl. Solutions of the diverse cations were prepared from their respective chlorides, and the diverse anions were prepared from their respective sodium salts (analytical grade). The sodium bromide and sodium iodide were analytical grade. Solvents were purified by standard methods.

A: X=H

B: X=CH$_2$COOEt (**L**)

Scheme 1.

Table 1. Effect of NaBr on the extraction of In(III) by **L** (In(III) = 50.0 μg/mL, **L** = 0.010 mol dm^{-3}, t = 25 °C)

NaBr (mol dm^{-3})	0.5	1.0	1.5	1.75	2.0
Ex% (%)	73.6	94.1	98.9	99.8	99.8

Chemical and physical measurements

Carbon and hydrogen were determined with a Carlo Erba 1106 elemental analyzer. Indium in the aqueous solution was determined by a spectrophotometric method using PAR as a photometric reagent and the amount of indium in the organic phase was determined by subtraction. In some experiments, the indium in the organic phase was stripped with 0.020 mol dm^{-3} HCl and then determined spectrophotometrically. A control experiment showed that shaking 2.0 mL of the organic phase containing 50.0 μg/mL of indium with 5.0 mL of 0.020 mol dm^{-3} aqueous HCl at 25 °C for 30 min, gave a stripping efficiency of 99.0%. The sodium was determined with a Plasma-Spec I inductively coupled plasma (ICP) emission spectrometer. IR spectra were recorded on a Perkin-Elmer FTIR-1750 spectrophotometer as a KBr pellet. Conductivity measurements were performed with a DOS-11A conductometer with a solute concentration of 1.0 $\times$ 10^{-3} mol dm^{-3} in methanol.

General procedure for the extraction of In(III)

Experiments were performed at 25 °C by mechanically shaking equal volumes (5.0 mL) of an aqueous solution containing indium(III) (50.0 μg/mL) and a certain amount of sodium bromide, and 1,2-dichloroethane containing from 0.0010 to 0.020 mol dm^{-3} of **L** for 30 min. The two phases were separated.

The distribution coefficient for the indium is defined as

$$D = [\text{In}]_{(o)}/[\text{In}].$$

The effect of competing ions on the extraction of indium was performed as follows. An aliquot of In^{3+} (50.0 μg/mL) solution containing 1.75 mol dm^{-3} of NaBr and varying amounts of diverse ions was extracted with an equal volume of 0.010 mol dm^{-3} **L** in 1,2-dichloroethane, as the proposed procedure. A portion of the organic phase (2.0 mL) was stripped with 5.0 mL of 0.020 mol dm^{-3} HCl and then determined spectrophotometrically. The tolerance limit for the competing ions was set at the amount which caused a $\pm2\%$ error in the recovery of indium.

Synthesis of the extracted complex

The solid complex was obtained by repeatedly extracting 5.0 mL of 0.30 mol dm^{-3} In(III) with an equal volume of 0.020 mol dm^{-3} **L** in 1,2-dichloroethane in the presence of 1.0 mol dm^{-3} of NaBr (saturated extraction). The aqueous phase was discarded and the organic phase was evaporated to near dryness at room temperature. The crude product thus obtained was dissolved in 1,2-dichloroethane. After filtration, the filtered solution was evaporated to dryness. The product was washed with diethyl ether and dried under vacuum for 24 h. Found: C, 49.96; H, 5.58; In, 8.06; Na, 1.59%. Calc. for C$_{60}$H$_{80}$O$_{12}$Br$_4$InNa: C, 49.68; H, 5.56; In, 7.79; Na, 1.59%.

The complex was recrystallized from chloroform-ethanol (1 : 3, V : V) by slow evaporation below 10 °C to obtain small transparent colorless crystals suitable for X-ray analysis.

X-ray structure determination

A colorless prismatic crystal of the title complex NaLInBr$_4$ with dimensions of 0.40 $\times$ 0.30 $\times$ 0.30 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). A total of 8043 reflections were collected and $I > 2\sigma$ reflections were 5305. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined. The final R factor was 0.0852 (R_w = 0.1619). The standard deviation of an observation of unit weight was 1.15. All calculations were performed using the teXsan crystallographic software package [13].

Results and discussion

Effect of NaBr on the extraction of In(III)

A preliminary experiment showed that In(III) in aqueous solution was hardly extracted by 0.010 mol dm^{-3} **L** only. Once NaBr was added to the aqueous solution, however, the extraction efficiency of In(III) increased greatly. The effect of NaBr on In(III) extraction is shown in Table 1. It is seen that the percentage extraction of indium reaches 99.8% with 0.010 mol dm^{-3} of **L** in the presence of 1.75 mol dm^{-3} of NaBr.

Effect of acidity on the extraction of In(III)

The extraction of In(III) (50.0 μg/mL) was performed at varying HCl concentrations (from 0.01 to 3.0 mol dm^{-3}) by 0.010 mol dm^{-3} of **L** in the presence of 1.75 mol dm^{-3} of NaBr. The results indicated that the extraction percentage of In(III) constant at $\geq98\%$ within this range of HCl concentrations.

Table 2. Atomic coordinates ($x \times 10^4$) and U^*(eq) for [Na**L**]InBr$_4$

Atom	x	y	z	U(eq)
In(1)	1731(1)	6969(1)	3736(1)	64(1)
Br(1)	1582(1)	6602(1)	4884(1)	128(1)
Br(2)	595(1)	7769(1)	3555(1)	132(1)
Br(3)	1342(1)	6156(1)	2967(1)	119(1)
Br(4)	3330(1)	7312(1)	3552(1)	108(1)
Na(1)	8081(2)	6832(1)	6056(1)	46(1)
O(1)	7792(3)	7238(2)	7176(2)	40(1)
O(2)	9069(3)	7730(2)	6029(2)	40(1)
O(3)	7692(3)	7198(2)	4921(2)	35(1)
O(4)	6359(3)	6695(2)	6082(2)	40(1)
O(5)	7905(3)	6097(2)	6916(2)	52(1)
O(6)	9655(3)	6740(2)	6646(2)	57(2)
O(7)	9036(3)	6423(2)	5218(2)	64(2)
O(8)	7262(4)	5861(2)	5421(2)	75(2)
O(9)	8517(3)	5904(2)	7935(2)	54(2)
O(10)	11143(3)	6974(2)	6530(2)	64(2)
O(11)	8833(3)	6010(2)	4213(2)	65(2)
O(12)	6393(4)	5170(2)	5854(3)	96(2)
C(1)	7362(4)	7748(3)	7403(3)	33(2)
C(2)	6423(5)	7720(3)	7520(2)	40(2)
C(3)	6007(5)	8221(3)	7766(3)	47(2)
C(4)	6477(5)	8728(3)	7875(3)	51(2)
C(5)	7415(5)	8734(3)	7746(3)	50(2)
C(6)	7874(4)	8247(3)	7488(3)	37(2)
C(7)	8873(4)	8309(3)	7273(3)	41(2)
C(8)	8899(4)	8330(3)	6012(3)	37(2)
C(9)	8865(4)	8630(3)	6612(3)	40(2)
C(10)	8764(4)	9232(3)	6588(3)	40(2)
C(11)	8644(4)	9538(3)	6001(3)	38(2)
C(12)	8638(4)	9211(3)	5418(3)	36(2)
C(13)	8756(4)	8607(3)	5399(3)	32(2)
C(14)	8660(4)	8286(3)	4747(3)	39(2)
C(15)	7181(4)	7674(3)	4672(3)	34(2)
C(16)	7637(4)	8194(3)	4546(2)	32(2)
C(17)	7118(4)	8647(3)	4264(3)	39(2)
C(18)	6166(4)	8593(3)	4101(3)	39(2)
C(19)	5743(4)	8074(3)	4258(3)	41(2)
C(20)	6219(4)	7619(3)	4560(3)	35(2)
C(21)	5679(4)	7099(3)	4802(3)	40(2)
C(22)	5635(4)	7102(3)	6065(3)	37(2)
C(23)	5229(4)	7263(3)	5447(3)	39(2)
C(24)	4479(4)	7619(3)	5430(3)	43(2)
C(25)	4103(4)	7835(3)	6006(3)	48(2)
C(26)	4535(5)	7678(3)	6618(3)	49(2)
C(27)	5297(4)	7310(3)	6658(3)	37(2)
C(28)	5808(4)	7203(3)	7327(3)	44(2)
C(29)	6023(5)	9290(3)	8105(3)	58(2)
C(30)	6197(9)	9768(5)	7707(7)	268(6)
C(31)	6144(10)	9370(6)	8802(4)	273(6)
C(32)	4951(7)	9241(6)	8030(7)	201(7)
C(33)	8455(4)	10181(3)	5979(3)	48(2)
C(34)	8617(7)	10491(4)	6657(4)	97(4)
C(35)	7420(6)	10260(4)	5752(5)	98(4)
C(36)	9058(6)	10503(4)	5474(4)	78(3)
C(37)	5621(4)	9121(3)	3807(3)	47(2)
C(38)	5495(6)	9558(4)	4352(4)	88(3)
C(39)	4642(5)	8951(4)	3552(4)	82(3)

Table 2. Continued

Atom	x	y	z	U(eq)
C(40)	6117(5)	9407(4)	3248(3)	86(3)
C(41)	3279(5)	8264(4)	5984(4)	59(2)
C(42)	3667(7)	8853(4)	5906(7)	167(6)
C(43)	2611(6)	8143(5)	5400(5)	134(5)
C(44)	2714(6)	8236(5)	6600(5)	152(5)
C(45)	8135(5)	6871(3)	7710(3)	47(2)
C(46)	8162(4)	6250(3)	7460(3)	36(2)
C(47)	8582(6)	5294(4)	7759(3)	66(3)
C(48)	8704(6)	4951(4)	8389(4)	83(3)
C(49)	10049(4)	7599(3)	6069(4)	55(2)
C(50)	10227(5)	7059(3)	6455(3)	43(2)
C(51)	11442(5)	6446(4)	6866(4)	86(3)
C(52)	12470(6)	6445(5)	6913(5)	129(5)
C(53)	8014(5)	6857(3)	4396(3)	46(2)
C(54)	8679(5)	6417(3)	4666(3)	51(2)
C(55)	9470(6)	5546(4)	4392(4)	82(3)
C(56)	9469(8)	5105(5)	3865(5)	136(5)
C(57)	6051(4)	6119(3)	6124(3)	44(2)
C(58)	6646(5)	5710(3)	5752(3)	49(2)
C(59)	6869(7)	4707(4)	5512(6)	120(4)
C(60)	6216(7)	4352(5)	5132(5)	134(5)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Stoichiometry of the extracted complex

Based on the above discussion, the overall extraction equilibrium between an aqueous solution containing In(III), Na$^+$, and Br$^-$ and an organic solution containing **L** may be expressed as:

$$Na^+ + In^{3+} + 4Br^- + n\mathbf{L}_{(o)} = Na\mathbf{L}_nInBr_{4(o)}. \qquad (1)$$

The extraction equilibrium constant can be written as

$$K_{ex} = [Na\mathbf{L}_nInBr_4]_{(o)}/[In^{3+}][Na^+][Br^-]_4[\mathbf{L}]_{(o)}^n, \qquad (2)$$

and the distribution ratio is then represented by

$$
\begin{aligned}
\log D &= \log [Na\mathbf{L}InBr_4]_{(o)}/[In^{3+}] \\
&= n \log [\mathbf{L}]_{(o)} + \log K_{ex}[Na^+] + 4 \log [Br^-].
\end{aligned} \qquad (3)
$$

At fixed concentrations of Na$^+$ and Br$^-$, the plot of $\log D$ versus $\log [\mathbf{L}]_o$ has a slope of 0.74 , and at fixed concentrations of Na$^+$ and $\mathbf{L}_{(o)}$, the plot of $\log D$ versus $\log [Br^-]$ has a slope of 3.34. The results reveal that the mole ratio of In^{3+} to **L** is not 1 : 1 and that of In^{3+} to Br$^-$ is not the expected value of 1 : 4. Therefore, the actual extraction is probably more complicated than that described in Equation (1).

Since Br$^-$ exhibits a certain degree of lipoplicity and ligand **L** is capable of forming a very stable complex with Na$^+$, the extraction of NaBr by **L** is possible. This point was confirmed by an extraction of 0.50 mol dm^{-3} of NaBr with 0.010 and 0.020 mol dm^{-3} **L** in 1,2-dichloroethane,

Table 3. Selected bond lengths (Å) and angles (°) for [NaL]InBr$_4$

In(1)—Br(1)	2.5015(13)	In(1)—Br(2)	2.5020(14)
In(1)—Br(3)	2.4973(14)	In(1)—Br(4)	2.4998(12)
Na(1)—O(1)	2.515(4)	Na(1)—O(2)	2.536(5)
Na(1)—O(3)	2.491(4)	Na(1)—O(4)	2.522(5)
Na(1)—O(5)	2.467(5)	Na(1)—O(6)	2.530(5)
Na(1)—O(7)	2.442(5)	Na(1)—O(8)	2.832(6)
Br(1)—In(1)—Br(2)	107.61(6)	Br(3)—In(1)-Br(1)	107.19(5)
Br(4)—In(1)—Br(1)	112.03(5)	Br(3)—In(1)-Br(2)	110.27(5)
Br(4)—In(1)—Br(2)	110.42(5)	Br(3)—In(1)-Br(4)	109.26(5)
O(1)—Na(1)—O(2)	80.32(15)	O(3)—Na(1)—O(2)	78.43(15)
O(3)—Na(1)—O(4)	83.45(15)	O(5)—Na(1)—O(4)	75.97(16)
O(5)—Na(1)—O(6)	74.40(16)	O(7)—Na(1)—O(6)	76.44(17)
O(7)—Na(1)—O(8)	67.13(17)	O(3)—Na(1)—O(1)	131.78(17)
O(1)—Na(1)—O(4)	79.43(15)	O(5)—Na(1)—O(1)	65.98(15)
O(1)—Na(1)—O(6)	78.10(16)	O(7)—Na(1)—O(1)	154.51(18)
O(1)—Na(1)—O(8)	128.65(17)	O(4)—Na(1)—O(2)	131.80(18)
O(5)—Na(1)—O(2)	131.82(16)	O(6)—Na(1)–O(2)	65.39(16)
O(7)—Na(1)—O(2)	87.97(18)	O(2)—Na(1)—O(8)	150.66(16)
O(5)—Na(1)—O(3)	149.73(18)	O(3)—Na(1)—O(6)	128.39(17)
O(7)—Na(1)—O(3)	66.35(15)	O(3)—Na(1)—O(8)	77.44(16)
O(4)—Na(1)—O(6)	148.16(17)	O(7)—Na(1)—O(4)	124.29(18)
O(4)—Na(1)—O(8)	61.04(15)	O(7)—Na(1)—O(5)	107.79(19)
O(15)—Na(1)—O(8)	73.24(16)	O(6)—Na(1)—O(8)	119.59(19)

Table 4. Least-squares planes for [NaL]InBr$_4$

Plane 1		Plane 2	
Atoms defining plane	Deviation (Å)	Atoms defining plane	Deviation (Å)
Na1	−1.0267	Na1	1.3896
O1	−0.0056	O5	−0.0449
O2	0.0057	O6	0.0466
O3	−0.0055	O7	−0.0482
O4	0.0055	O8	0.0465
Mean deviation from plane = 0.0056 Å		Mean deviation from plane = 0.0466 Å	

which shows the extraction of 1.40×10^{-4} and 2.11×10^{-4} mol dm^{-3} of NaBr, respectively. The detection of both In(III) and NaBr in the organic phase after the extraction of In(III) in the presence of 0.50 mol dm^{-3} of NaBr containing 50 μg/mL of In(III) in aqueous phase revealed that 2.80×10^{-4} mol dm^{-3} of In(III) and 4.0×10^{-4} mol dm^{-3} of Na$^+$ were extracted by 0.010 mol dm^{-3} **L**. The results suggest that **L** extracts both NaLInBr$_4$ and NaLBr. The simultaneous presence of two extracted species in the organic phase leads to a lower concentration of free ligand [**L**]$_{(0)}$ than if there is only one extracted species of NaLInBr$_4$. The ratio of [NaLInBr$_4$] to [NaLBr] in the organic phase should decrease as the concentration of **L** or Br$^-$ increases. Thus, the possibility for formation of the extracted species NaLBr at higher concentration of **L**$_0$ or Br$^-$ is greater than that at the lower concentrations. As a result, the slopes of the plots of log D vs. log [**L**]$_o$ and [Br$^-$] should be smaller than the expected values of 1 and 4.

If the coexistence of these two extracted species in the organic solution is considered, [**L**]$_{(o)}$ cannot be accurately determined due to the uncertainty in the amount of NaLBr$_{(o)}$. As a result, the Kex value which is defined as Kex = [NaLInBr$_4$]$_{(o)}$/[In^{3+}][Na$^+$][Br$^-$]^4[**L**]$_{(o)}$ cannot be determined. However, it has been confirmed that the stoichiometry of the solid extracted species is NaLInBr$_4$ by the saturated-extraction method. This result suggests that the extracted species NaLBr may occur in the initial extraction stage, but probably is replaced gradually by the more lipophilic species NaLInBr$_4$ in the course of saturated extraction. Finally, the extracted species NaLInBr$_4$ predominates in the organic phase.

Effects of competing ions on the extraction of In(III)

Extraction of In(III) was performed as before, but in the presence of large amounts of competing ions. The results show that Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, and Ca^{2+} have no effect on In(III) extraction at a ratio of 1 : 500. The toler-
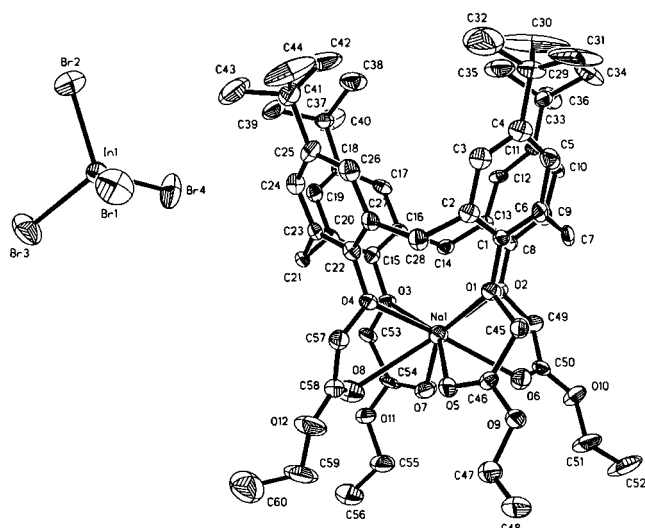
Figure 1. Structure of [NaL]InBr$_4$. Hydrogen atoms are omitted for clarity.

Figure 2. The molecular packing arrangement in the cell.

ance limit for Cr^{3+} is 1 : 50 and those for Al^{3+} and Fe^{2+} are 1 : 30. Most anions such as NO$_3^-$, SO$_4^{2-}$, and Cl$^-$ can also be tolerated at a ratio of 1 : 500. The anion SCN$^-$ is tolerated at a ratio of 1 : 60 and both ClO$_4^-$ and Cit^{3-} are tolerated at a ratio of 1 : 15. Therefore, it is demonstrated that the proposed extraction system exhibits highly selective extraction of In(III) in the presence of large amounts of competing ions.

Characterization of solid extracted complex

To further elucidate the mechanism of this solvent extraction system, the solid extracted complex was characterized by IR spectra and conductivity measurements and its crystal structure was determined by X-ray diffraction analysis.

The IR spectrum of the solid extracted complex showed a new strong absorption band at 1746 cm^{-1}. Since the characteristic absorption bands of the carbonyl group in the free ligand are at 1735 and 1762 cm^{-1}, this change in the IR spectrum indicates that the Na$^+$ is bound to carbonyl oxygen atoms of the ligand molecule [2].

The molar conductance of the complex NaLInBr$_4$ was determined in anhydrous methanol. The λ_M value of 118 S cm^2 mol^{-1} indicates a 1 : 1 electrolyte [14], suggesting that the complex is composed of [NaL]$^+$ and InBr$_4^-$. These results are consistent with those reported for the solid extracted complex NaLReO$_4$·H$_2$O [8].

Molecular and crystal structure of the complex

Crystal data: C$_{60}$H$_{80}$O$_{12}$Br$_4$InNa, Fw = 1450.69, monoclinic, space group P2$_1$/c, a = 14.504(3), b = 23.270(5), c = 20.290(4) Å, β = 93.02(3)°, V = 6839(2) Å^3, Z = 4, Dc = 1.409 g/cm^3, F(000) = 2944.

The crystal structure of NaLInBr$_4$ is illustrated in Figure 1. Figure 2 shows the molecular packing arrangement in the unit cell. Atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3, respectively.

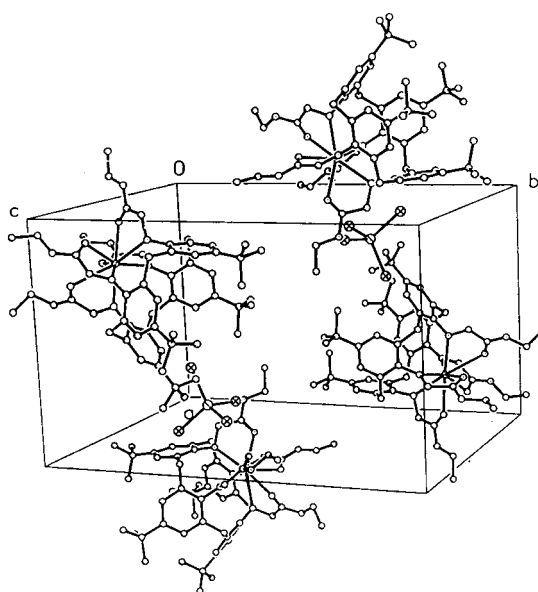The structure of the complex NaLInBr$_4$ consists of [NaL]$^+$ units and non-coordinated InBr$_4^-$ anions. The Na$^+$ lies between two planes formed by four ether (plane 1) and four carbonyl oxygen atoms (plane 2), respectively. Planes 1 and 2 (Table 3) are almost parallel and the dihedral angle between them is 3.1°. The distances of all coordinated oxygen atoms and Na$^+$ to the least-squares planes 1 and 2 are listed in Table 3. All eight oxygen atoms are directed inwards and bind the sodium ion, the coordination number of sodium is eight. The Na—O bond distances varied from 2.442 to 2.832 Å. The interplanar angles between the individual benzene rings and the plane of the four methylene carbon atoms (C7, C14, C21, C28) are 111.9°, 114.2°, 69.0° and 67.0°, respectively.

The In(III) exists in the form of the tetrabromoindate complex anion InBr$_4^-$. The In—Br distances vary from 2.497 to 2.502 Å, and the average distance is 2.500 Å. The Br—In—Br angles vary from 107.19 to 112.03°. Therefore, the tetrabromoindate group has an approximately tetrahedral configuration. The distance between In and Na is 7.28 Å.

Conclusions

The hydrophobic anionic complex InBr$_4^-$ is easily extracted into an organic phase by the pre-organized cationic complex NaL through the formation of the hydrophobic ion-pair NaLInBr$_4$. The presence of a certain amount of NaBr is necessary for the extraction in two aspects. First, the Na$^+$ is bound to **L** to form a stable complex NaL$^+$ which is predominant in the extraction process. Second, the Br$^-$ transforms the In(III) into an extractable anionic form of InBr$_4^-$. In such an extraction system, the targeted anion InBr$_4^-$ can be separated from the other hydrophilic cations and anions. These results suggest the development of further applications of the pre-organized cationic complex NaL$^+$ for the extraction of other cations which can be transformed into hydrophobic anionic complexes. Such investigations are now in progress.

34

References

1. S.K. Chang and I. Cho: *J. Chem. Soc., Perkin Trans. I* 211 (1986).
2. A. Arduini, A. Pochini, S. Reverberi, R. Ungaro, G.D. Andreetti and F. Ugozzoli: *Tetrahedron* **42**, 2089 (1986).
3. G. Ferguson, B. Kaitner, M.A. Mckervey and E.M. Seward: *J. Chem. Soc., Chem. Commun.* 584 (1987).
4. M.J.S. Weill, F.A. Neu and E. Marques: *Pure Appl. Chem.* **61**, 1597 (1989).
5. F. Arnaud-Neu, E.M. Collins, M. Deasy, G. Ferguson, S.J. Harris, B. Kaitner, A. Lough, M.A. McKervey, E. Marques, B.I. Ruhl, M.J. Schwing-Weill and E.M. Seward: *J. Am. Chem. Soc.* **111**, 8681 (1989).
6. K. Iwamoto and S. Shinkai: *J. Org. Chem.* **57**, 7066 (1992).
7. A. Arduini, A. Pochini, S. Reverberi and R. Ungaro: *Tetrahedron* **42**, 2089 (1986).
8. Z. Zhou, Y. Xing and Y. Wu: *J. Incl. Phenom. Mol. Recog. Chem.* **34**, 219 (1999).
9. Z.-X. Zhou and X.-X. Zhang: *Acta Chim. Sin. (Huaxue Xuebao)* **46**, 496 (1988); *Chem. Abstr.* **109**, 136000b (1988).
10. Z.-X. Zhou and X.-X. Zhang: *Acta Chim. Sin. (Huaxue Xuebao)* **44**, 870 (1986); *Chem. Abstr.* **106**, 11399v (1987).
11. R.G. Vibhute and S.M. Khopkar: *Chem. Anal. (Warsaw)* **37**, 15 (1992).
12. C.D. Gutsche and M. Iqbal: *Org. Synth.* **68**, 234 (1989).
13. Single Crystal Structure Analysis Software, Version 1, 6 (1993); Molecular Structure Corporation, The Woodlands, TX.
14. W.J. Geary: *Coord. Chem. Rev.* **7**, 81 (1971).