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

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Abstract. The extraction of perrhenate with 25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-*p*-*tert*-butylcalix[4]arene (**L**) into 1,2-dichloroethane was investigated. The presence of Na^+ in the aqueous phase is necessary for the extraction. The extraction equilibrium has been established and the thermodynamic quantities $\Delta H°$, $T\Delta S°$ and $\log K_{ex}$ are −61.3 kJ/mol, −41.4 kJ/mol and 3.69, respectively. The effect of diverse ions on the extraction of ReO_4^- was studied. The corresponding extracted complex $[Na\mathbf{L}]ReO_4 \cdot H_2O$ was prepared and characterized by EA, IR and X-ray structure analysis. The complex crystallizes in the tetragonal space group $P4/ncc$ with $a = b = 14.735(3)$, $c = 29.094(3)$ Å, $V = 6316(2)$ Å^3, $Z = 4$.

Key words: extraction, perrhenate, calix[4]arene, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82255 (19 pages).

1. Introduction

Calixarene derivatives have been attracting much attention as a novel type of macrocyclic host compound [1–4]. Their high recognition both of metallic or organic ions and neutral molecules is one of their remarkable features as a specific receptor.

Among the great diversity of calixarene derivatives, the calix[4]arene esters exhibit remarkable ability to recognize and discriminate metal ions [5–10]. The cryptand-like hydrophilic region, consisting of a cavity made of oxygen atoms from the original phenol and of carbonyl oxygens, is particularly well adapted for the complexation of alkali metal cations, especially sodium ion, that is, a sodium ion can form a stable cationic complex with calix[4]arene ethyl ester.

The excellent complexation property of crown ethers with alkali metal ions has been used to extract some anionic species containing several interesting elements [11–17], and our previous studies have also shown that the association of the alkali

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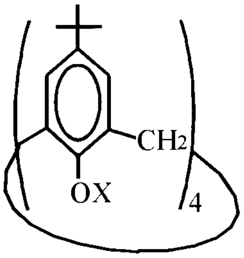

A: X=H
B: X=CH_2COOEt (**L**)

Formula 1.

metal ion–crown ether cationic complex with the univalent anion, ReO_4^- [18, 19], or metallic complex anions, $InBr_4^-$ [20], InI_4^- [20], and $AuCl_4^-$ [21] to form ion-pair species can be easily extracted into the organic phase. Since the title ligand (**L**) has an extension of the lipophilic calix defined by the aromatic nuclei and the four *p-tert*-butyl groups, the hydrophobic character of **L** is stronger than that of a crown ether. The extraction of ReO_4^- by **L** in the presence of Na^+ was thus examined and some satisfactory results were obtained. The extraction equilibrium may be expressed as follows:

$$Na^+ + ReO_4^- + n\mathbf{L}_{(o)} \rightleftharpoons Na\mathbf{L}_n ReO_{4(o)}$$

where the subscript 'o' denotes the organic phase and its absence refers to the aqueous phase.

It shows that the presence of Na^+ in aqueous solution is necessary for the formation of the hydrophobic extracted complex which can be extracted quantitatively into the organic phase. This extraction system is also very useful for the separation and extraction of a micro-amount of ReO_4^- from large amounts of many cations such as Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Ni^{2+} etc., and anions such as MoO_4^{2-}, Cl^-, Br^-, NO_3^-, Ac^- etc., as these cations and anions exhibit hydrophilic character. In order to further elucidate the mechanism of the extraction of ReO_4^- by **L** in the presence of Na^+, the extracted complex was prepared and characterized by X-ray structural analysis.

2. Experimental

2.1. REAGENTS

p-tert-Butylcalix[4]arene (A) and *cone*-25,26,27,28-tetrakis[(ethoxycarbonyl) methoxy]-*p-tert*-butylcalix[4]arene [**L**] (B) were synthesized according to the literature methods [9, 22]. The standard rhenium solution was prepared by dissolving solid $KReO_4$ (99.9% pure) in distilled water. Solutions of sodium, potassium, ammonium and other diverse cations were prepared from their respective sulphates (analytical grade), and the diverse anions were prepared from their respective sodium salts (the VO_3^- was added as ammonium salt). All solvents used were purified by standard methods.

2.2. CHEMICAL AND PHYSICAL MEASUREMENTS

Elemental analyses were determined on a Carlo Erba 1106 elemental analyser. The rhenium in the aqueous phase was determined spectrophotometrically in benzene by the butylrhodamine B method [23] and the amount of rhenium in the organic phase was determined by subtraction. The sodium was determined on a Plasma-Spec I inductively coupled plasma (ICP) emission spectrometer. An infrared spectrum was recorded on a Perkin-Elmer FTIR-1750 spectrophotometer as a KBr pellet. The conductance measurement was carried out using a DDS-11A conductometer with a solute concentration of 1.0×10^{-3} mol dm^{-3} in methanol.

2.3. GENERAL PROCEDURE FOR EXTRACTION OF ReO_4^-

An aqueous solution containing ReO_4^- (Re taken = 100.0 μg/ml) and 0.50–4.0 mol dm^{-3} of M^+ ($M^+ = Na^+, K^+, NH_4^+$) and an equal volume of 1,2-dichloroethane containing 2.0×10^{-3}–5.0×10^{-2} mol dm^{-3} of **L** were placed in a stoppered glass tube and mechanically shaken for 30 min at 20 ± 0.1 °C and then centrifuged for 5–10 min to separate the two phases.

The distribution ratio of the rhenium was defined as

$$D = [Re]_{(o)}/[Re]$$

For the determination of thermodynamic quantities, the extractions were performed at 20, 25, 30, 36 and 40 ± 0.1 °C.

The effect of diverse ions on the extraction of perrhenate was performed as follows. An aliquot of ReO_4^- (Re taken = 50.0 μg/mL) solution containing 0.50 mol dm^{-3} Na_2SO_4 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. The separated organic phase (1 mL) was placed in a stoppered glass tube and mechanically shaken for 10 min at 20 ± 0.1 °C with 20.0 mL strip liquor (per 100.0 mL of strip liquor contain 24.0 mL of concentrated hydrochloric acid, 12.0 mL of 5% thiourea solution and 6.0 mL of 1 mol dm^{-3} stannous chloride in 4 mol dm^{-3} hydrochloric acid solution). After 40 min, the absorbance was measured at 395 nm, and rhenium was determined by referring to the calibration curve which is linear in the range of 0.0–50.0 μg/mL of rhenium [24]. The tolerance limit of the diverse ions was set at the amount required causing ±2% error in the recovery of rhenium by the proposed method.

2.4. SYNTHESIS OF THE EXTRACTED COMPLEX

The solid extracted complex was obtained by repeatedly extracting 0.030 mol dm^{-3} ReO_4^- with 0.010 mol dm^{-3} **L**-1,2-dichloroethane in the presence of 0.25 mol dm^{-3} Na_2SO_4 (saturated extraction). The aqueous phase was discarded and the organic phase of 1,2-dichloroethane was evaporated to near dryness. The crude powder was washed with anhydrous methanol and dried in vacuum for 24 h. *Found*: C, 56.69; H, 6.42; Na, 1.90; Re, 14.60. *Calc. for* $C_{60}H_{82}O_{17}NaRe$: C, 56.10; H, 6.44; Na, 1.79; Re, 14.50.

As compared with the above saturated extraction method for preparing the extracted complex, a convenient method (one-time extraction) was suggested as follows. The 0.030 mol dm^{-3} ReO_4^- was extracted only once with 0.010 mol dm^{-3} **L**-1,2-dichloroethane in the presence of 0.50 mol dm^{-3} Na^+ and then the organic phase was evaporated to near dryness. The residue contained the complex and the unreacted ligand. After the residue was extracted by diethyl ether, the pure product was obtained and the yield was 90%. *Found*: C, 56.23; H, 6.34; Na, 1.67; Re, 14.55. The analytical data show that this product has the same composition as that prepared by the saturated extraction method.

The solid complex was recrystallized from a methanolic solution by slow evaporation below 10 °C to obtain the small transparent colorless plate crystals suitable for X-ray analyhsis.

2.5. X-RAY STRUCTURE DETERMINATION

A colorless plate crystal of the title complex with approximate dimensions of 0.20 × 0.20 × 0.30 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7106$ Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting of 25 carefully centered reflections in the range $13.60 < 2\theta < 21.22°$. The data were collected using the ω–2θ scan technique. A total of 3261 reflections was collected, and 1452 reflections were observed reflections [$I > 3.00\sigma(I)$]. The data were corrected for Lorenz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques and refined by a full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R factor was 0.043 ($R_W = 0.056$). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

Table I. Effects of Na^+, K^+ and NH_4^+ on the extraction of ReO_4^- with **L** (Re = 100.0 μg/mL, solvent used 1,2-dichloroethane)

$[M^+]$ (mol dm^{-3})		[L] (mol dm^{-3})	*E* (%)
Na^+	0.00	0.010 **L**	2.7
	0.50	0.010 **L**	93.1
	1.00	0.010 **L**	99.0
K^+	1.00	0.020 **L**	14.3
	1.00	0.050 **L**	28.2
	0.50	0.010 B15C5	87.3[a]
	0.50	0.050 B15C5	~100[a]
NH_4^+	4.00	0.050 **L**	4.0

[a] Ref. [19].

3. Results and Discussion

3.1. EFFECTS OF UNIVALENT CATIONS ON THE EXTRACTION OF ReO_4^-

The preliminary experiment showed that ReO_4^- was hardly extracted by 0.010 mol dm^{-3} **L** in the absence of M^+ ($M^+ = Na^+$, K^+ and NH_4^+). However, once a certain amount of Na^+ was added into the aqueous solution, the extraction efficiency of ReO_4^- was increased greatly. The extraction of ReO_4^- is nearly quantitative by 0.010 mol dm^{-3} **L** and in the presence of 1.0 mol dm^{-3} Na^+. As compared with the effects of Na^+ on the extraction of ReO_4^-, the effects of K^+ and NH_4^+ were also examined. The results are listed in Table I.

It is obvious that the addition of Na^+ to the aqueous solution is necessary for the extraction of ReO_4^- with **L**, and Na^+ is more efficient than K^+ or NH_4^+. Therefore, from a practical point of view, the following discussions were only concerned with the extraction of ReO_4^- with **L** in the presence of Na^+.

Table I also reports some data for B15C5. By comparing the results between the Na^+–**L** system and the K^+–B15C5 system, it can be seen that the extractability of **L** for ReO_4^- is higher than that of B15C5 under the same concentration of M^+ and of extractant (in 1,2-dichloroethane). This difference may be attributable to the higher expected lipophilicity of **L** with respect to B15C5.

3.2. STOICHIOMETRY OF THE EXTRACTED SPECIES AND THE K_{ex} VALUE

Based on the above experiment, the extraction equilibrium between an aqueous solution containing ReO_4^- and Na^+ and an organic solution containing **L** could be expressed as

$$Na^+ + ReO_4^- + n\mathbf{L}_{(o)} \rightleftharpoons Na\mathbf{L}_n ReO_{4(o)}.$$

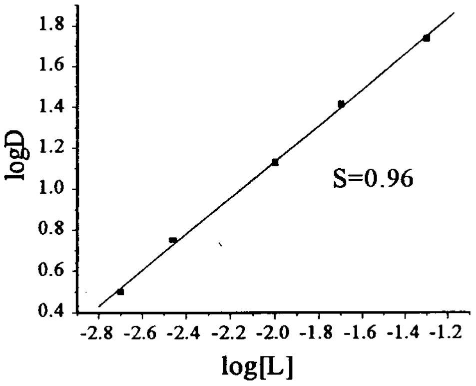

Figure 1. Distribution ratio of ReO_4^- as a function of **L** concentration, ($[Na^+]$ = 0.50 mol dm^{-3}, T = 293 K).

The extraction equilibrium constant can be written as

$$K_{ex} = [Na\mathbf{L}_nReO_4]_{(o)}/[ReO_4^-][Na^+][\mathbf{L}]^n_{(o)} = D/[Na^+][\mathbf{L}]^n_{(o)}$$

and the distribution ratio is then represented by

$$\log D = n \log[\mathbf{L}]_{(o)} + \log\{K_{ex}[Na^+]\}.$$

Plots of log D versus $\log[\mathbf{L}]_{(o)}$ at a fixed concentration of Na^+ had a slope of 0.960 (Figure 1). Therefore the molar ratio of Re : **L** is 1 : 1 and the extracted species is $[Na\mathbf{L}][ReO_4]$. The log K_{ex} (20 °C) calculated from the data in Figure 1 is 3.69.

3.3. THERMODYNAMIC QUANTITIES

The K_{ex} value increases with decreasing temperature. The plot of log K_{ex} against $1/T$ shows a linear relationship for the extraction system (Figure 2). The enthalpy change (ΔH°) was calculated from the slope of the straight line by using the following equation: $\ln K_{ex} = -\Delta H^\circ/RT + \Delta S^\circ/R$. The entropy change ($\Delta S^\circ$) was calculated from the ΔH° and K_{ex} values. The thermodynamic quantities are listed as follows, together with the log K_{ex} value determined at 20 °C (Figure 1):

$$\log K_{ex} = 3.69, \quad \Delta H^\circ = -61.3 \text{ kJ/mol}, \quad T\Delta S^\circ = -41.4 \text{ kJ/mol}.$$

The large negative ΔH° value indicates that the extraction reaction is exothermic. Since the ΔS° value is also negative, the extraction of ReO_4^- by the cationic complex $[Na\mathbf{L}]^+$ is therefore enthalpy driven.

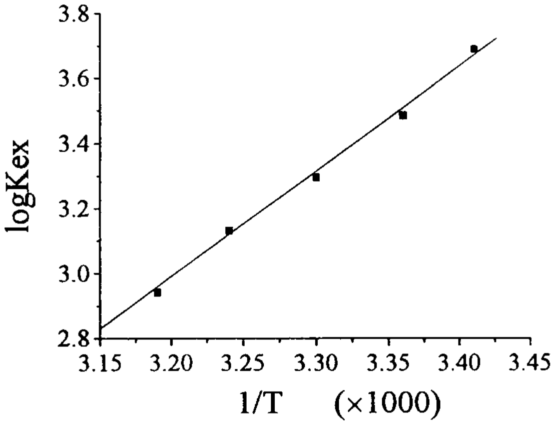

Figure 2. Plots of log K_{ex} against $1/T$.

Table II. Effect of diverse ions on the extraction of ReO_4^- with **L** (Re taken = 50.0 μg/mL)

Diverse ions	Ratio	Amount tolerated (μg)
Mg^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, MoO_4^-	1 : 1000	50,000
Al^{3+a}, Cl^-, Br^-, Ac^{-b}, VO_3^-, $EDTA^{2-}$, Cit^{3-c}, PO_4^{3-}	1 : 500	25,000
NO_3^-	1 : 400	20,000
SCN^-, Sal^{-d}	1 : 20	1,000
ClO_4^-	1 : 5	250

[a] The ratio of Re : Al^{3+} can only reach 1 : 500, owing to the solubility.
[b] Ac = acetate. [c] Cit = citrate. [d] Sal = salicylate.

3.4. EFFECTS OF DIVERSE IONS AND ACIDITY ON THE EXTRACTION OF ReO_4^-

ReO_4^- was extracted by the above proposed extraction system in the presence of a large amount of diverse ions (Table II). It was possible to carry out actual separations. The data show that diverse metal ions such as Mg, Cr, Mo (as MoO_4^{2-}), Fe, Ni, Zn, Cd, Cu etc. are tolerated in the ratio of 1 : 1000, while for Al and V (as VO_3^-) the ratio is 1 : 500. Most anions such as Cl^-, Br^-, Ac^-, $EDTA^{2-}$, Cit^{3-}, PO_4^{3-} can also be tolerated in the ratio of 1 : 500. NO_3^- is tolerated in the ratio of 1 : 400. ClO_4^-, and both SCN^- and Sal^- are tolerated in the lower ratio of 1 : 5, 1 : 20 and 1 : 20, respectively. Therefore, it can be concluded that the proposed extraction system exhibits highly selective extraction for ReO_4^- in the presence of a large amount of diverse ions.

The results of the effect of the acidity of the aqueous phase are shown in Figure 3. It has been shown that the extraction efficiency of ReO_4^- was not affected while the pH increased from 1 to 12.

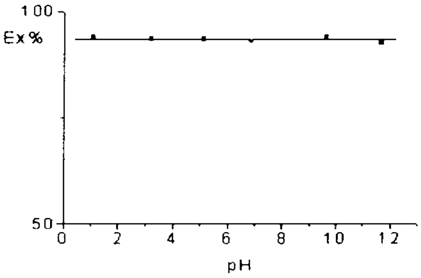

Figure 3. Effect of acidity on the extraction of ReO_4^- ($[Na^+]$ = 0.50 mol dm^{-3}, [Re] = 100.0 μg/mL).

3.5. CHARACTERIZATION OF THE SOLID EXTRACTED COMPLEX

IR spectra of the characteristic frequencies of the carbonyl of the free ligand at 1735 and 1762 cm^{-1} are substituted by a new strong absorption band at 1747 cm^{-1} for the extracted complex. This indicates that the Na^+ is bound to carbonyl oxygen atoms of the ligand molecule [6]. As compared to potassium perrhenate, the similar strong absorption at 906 cm^{-1} in the extracted complex which is attributed to a ReO_4^- stretching vibration can be observed, indicating that there exists the same form of ReO_4^- [25]. The IR spectrum also exhibited an obvious absorption peak of the water molecule at 3471 cm^{-1}, which is consistent with the results of elemental analyses.

The molar conductance of the title complex was determined in anhydrous methanol. The Λ_M value is 84.0 S cm^2 mol^{-1}, which can be classified as a 1 : 1 electrolyte [26]. This implies that the title complex may be formed of $[Na\mathbf{L}]^+$ and ReO_4^-.

3.6. MOLECULAR AND CRYSTAL STRUCTURE OF THE EXTRACTED COMPLEX

Crystal Data: $C_{60}H_{82}O_{17}NaRe$, F_W = 1284.49, tetragonal, space group $P4/ncc$, $a = b$ = 14.735(3) Å, c = 29.094(3) Å, V = 6316(2) Å^3, Z = 4. $F(000)$ = 2640.00, $\mu(MoK_\alpha)$ = 19.96 cm^{-1}. R = 0.043, R_W = 0.056.

The structure of $[Na\mathbf{L}]ReO_4 \cdot H_2O$ is illustrated in Figure 4. Figure 5 shows the molecular packing arrangement in the unit cell. The atomic coordinates, selected bond lengths and angles are given in Table III.

The structure of the title complex consists of $[Na\mathbf{L}]^+$ units, non-coordinated perrhenate anions and structural water molecules. The conformation of **L** in $[Na\mathbf{L}]^+$, which exhibits crystallographic $C4$ symmetry, is more regular than that of the free ligand. The Na^+ lies between two distinct parallel planes formed by four ether and four carbonyl oxygen atoms, respectively. All eight oxygen atoms are directed inwards and form bonds to the sodium. The coordination polyhedron is a tetragonal antiprism as shown in Figure 6, which indicates that the Na^+ is octacoordinated. The Na—O bond distances are 2.461(5) Å and 2.599(7) Å for the ether and car-

Table III(a). Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

Atom	*x*	*y*	*z*	B_{eq}
Re	0.7500	0.2500	0.0000	4.106(9)
Na	0.7500	−0.2500	−0.0762(2)	3.65(7)
O(1)	0.8378(4)	0.2874(5)	0.0337(3)	7.0(2)
O(2)	0.7969(3)	−0.1045(3)	−0.0422(2)	2.9(1)
O(3)	0.7261(4)	−0.1085(4)	−0.1282(2)	4.9(2)
O(4)	0.8303(4)	−0.0079(4)	−0.1520(2)	5.2(2)
O(5)	0.2500	0.2500	0.393(1)	18.1(7)
C(1)	0.7881(6)	−0.0583(6)	−0.1204(3)	3.9(2)
C(2)	0.8283(5)	−0.0374(5)	−0.0740(3)	3.7(2)
C(3)	0.8069(5)	−0.0736(4)	0.0035(3)	2.7(2)
C(4)	0.7331(5)	−0.0331(5)	0.0245(3)	2.9(2)
C(5)	0.7470(6)	0.0054(5)	0.0679(2)	3.3(2)
C(6)	0.8299(6)	0.0010(5)	0.0900(3)	3.3(2)
C(7)	0.9002(5)	−0.0434(5)	0.0682(3)	3.1(2)
C(8)	0.8907(5)	−0.0826(5)	0.0244(2)	2.8(2)
C(9)	0.9688(5)	−0.1380(5)	0.0030(3)	3.3(2)
C(10)	0.8420(6)	0.0468(6)	0.1368(3)	4.1(2)
C(11)	0.764(1)	0.052(3)	0.1628(6)	28(1)
C(12)	0.914(2)	0.012(2)	0.1635(5)	26(1)
C(13)	0.860(2)	0.139(1)	0.1323(5)	25(1)
C(14)	0.794(1)	−0.018(1)	−0.1991(4)	8.5(4)
C(15)	0.840(2)	−0.076(2)	−0.220(1)	10(1)
C(15′)	0.857(3)	0.025(3)	−0.2265(9)	18(1)

Table III(b). Selected bond lengths (Å) and angles (°)

Re—O(1)	1.714(7)	Na—O(2)	2.461(5)
Na—O(3)	2.599(7)		
Re—O(1)—O(1)	109.1(2)	O(1)—Re—O(1)	110.2(5)
Na—O(2)—O(2)	80.7(1)	O(2)—Na—O(2)	132.6(3)
Na—O(2)—O(3)	64.7(2)	O(2)—Na—O(3)	125.2(2)
Na—O(2)—O(3)	153.5(2)	O(2)—Na—O(3)	83.7(2)
Na—O(3)—O(3)	70.2(2)	O(2)—Na—O(2)	108.9(3)

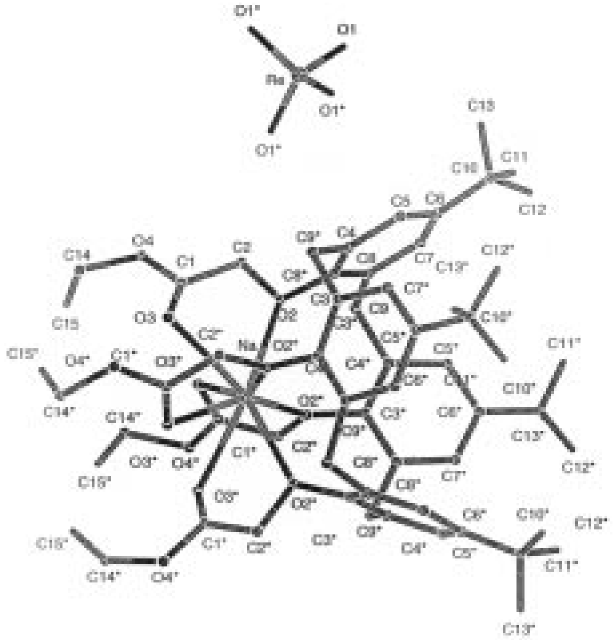

Figure 4. Structure of $[Na\mathbf{L}]ReO_4 \cdot H_2O$. The water molecule is omitted for clarity. All 15 carbon atoms of **L** are represented by the thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table IV. Least squares planes

Plane number 1		Plane number 2	
Atoms defining plane	Distance (Å)	Atoms defining plane	Distance (Å)
C(3)	0.021(7)	Na	0.025(2)
C(4)	−0.017(7)	O(2)	−0.182(5)
C(5)	0.002(7)	O(3)	−0.239(6)
C(6)	0.010(7)	C(1)	0.343(9)
C(7)	−0.006(7)	C(2)	0.337(8)
C(8)	−0.010(7)		

bonyl oxygen atoms, respectively. The least squares planes of the aryl planes and the O(2)—C(2)—C(1)—O(3)–Na planes are shown in Table IV. The dihedral angle between the two planes is 78.53°.

The perrhenate group has a tetrahedral configuration with the following dimensions: Re—O = 1.714(7) Å, ∠O—Re—O = 109.1(2) or 110.2(5)°. Since the distance between the sodium and rhenium atoms is 7.69 Å, the complex cation $[Na\mathbf{L}]^+$ and anion ReO_4^- are linked by electrostatic attraction to form an ion-pair

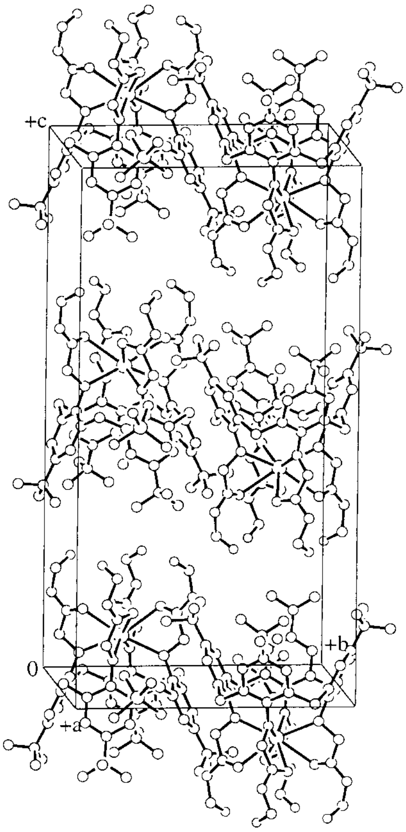

Figure 5. The molecular packing arrangement in the unit cell.

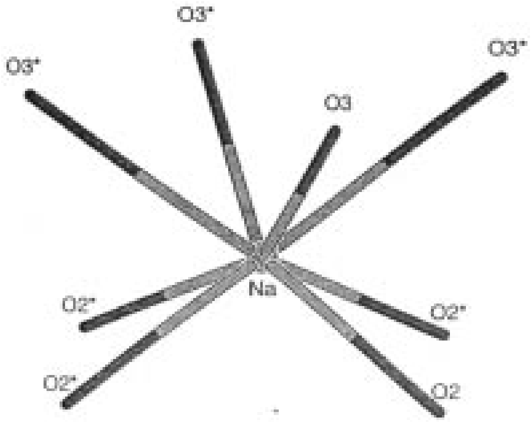

Figure 6. The coordination polyhedron of sodium ion in the complex.

which is consistent with those as observed in the IR spectra of ReO_4^- and with the molar conductance of the title complex.

Although the crystals were obtained from the anhydrous methanolic solution, there still exist structural water molecules which play a crucial role in stabilizing the lattice.

4. Conclusions

From the above discussion, a new extraction system for the separation of ReO_4^- from large amounts of diverse ions is offered. X-ray structural analysis reveals that the extracted complex exhibits lipophilic character suggesting that the ligand **L** may be used as a new extractant for the extraction of univalent lipophilic anions or complex anions in the presence of Na^+. To our knowledge, single crystals containing [Na**L**]$^+$ have not previously been obtained, and this paper is the first to report the crystallographic characterization of the [Na**L**]$^+$ cation.

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