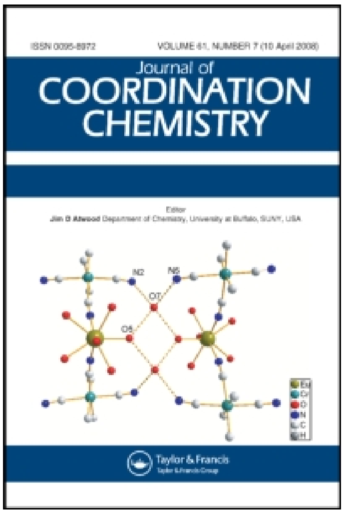

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Complexation and extraction studies of lanthanide ions by 1,1'-(3,6,9-Trioxaundecanedionyl)Diphenothiazine

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COMPLEXATION AND EXTRACTION STUDIES OF LANTHANIDE IONS BY 1,1′-(3,6,9-TRIOXAUNDECANEDIONYL)DIPHENOTHIAZINE

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Solid complexes of lanthanide picrates with 1,1′-(3,6,9-trioxaundecanedionyl)diphenothiazine (L), [Ln(pic)$_3$L] (Ln = La, Nd, Eu, Gd, Er, Y), have been prepared and characterized by elemental analysis, IR and ^{1}H NMR spectra. The molecular structure of [Er(pic)$_3$L]$\cdot$1/2C$_2$H$_5$OH shows that five oxygens of L form a ring-like coordination structure. Er(III) is 9-coordinated by L together with the other two unidentate and one bidentate picrate anions, revealing a tri-capped distorted trigonal prism geometry. Solvent extraction of Ln(III) with L has been carried out in a water–nitrobenzene system by use of the multitracer method. The relationship between the complex structure and extractabilities of the ligand is discussed.

Keywords: Lanthanide picrate; Open-chain crown ether; Crystal structure; Extraction

INTRODUCTION

Glycol-*O*,*O*′-diacetamide compounds have been widely studied in connection with extraction of lanthanide or some actinide ions, and in ion-selective electrodes [1–4]. The rare earth complexes and extraction studies of this type of compound have been reported, among which *N*,*N*,*N*′,*N*′-tetraphenyl-3,6-dioxaoctanediamide shows a high extraction ability towards light lanthanides. This property depends on a ring-like coordination structure and the terminal group effect [5–9]. As a further study of such ligands, to promote the design of better extractants and further exploration of the relationship between structure and property, we describe here the solvent extraction of lanthanide picrates with 1,1′-(3,6,9-trioxaundecanedionyl)diphenothiazine and the structure of its erbium picrate complex.

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EXPERIMENTAL

Materials

The lanthanide picrate [10] and L [11] were prepared according to literature methods. All chemicals were of AR grade and used without further purification. ^{152}Eu(III) was purchased from China National Nuclear Corporation.

General Preparation of the Complexes

A solution of 0.1 mmol L in 15 cm^3 of absolute alcohol was added dropwise to a solution of 0.1 mmol lanthanide picrate in 20 cm^3 of absolute alcohol. The mixture was stirred at room temperature for 4 h. The precipitated solid complex was filtered, washed with absolute alcohol and then dried *in vacuo* over P_4O_{10} for 48 h. A transparent single crystal of the erbium complex was grown from CH_3CN by slow evaporation at room temperature over approximately one month.

Chemical and Physical Measurements

The metal ions were determined by EDTA titration using xylenal orange as an indicator. C, N and H were determined using a Vario EL elemental analyser. IR spectra were recorded on a Nicolet avatar 360 FT-IR instrument using KBr discs in the 400–4000 cm^{-1} region, ^{1}H NMR spectra were measured on a Brucker AC 80 spectrometer in CD_3COCD_3 solution with TMS as internal standard.

X-ray Crystallography

For the erbium complex, X-ray measurements were performed on a P4 four-circle diffractometer with graphite-monochromated Mo Kα radiation at 296(2) K. The structure was solved by direct methods and refined by full-matrix least-squares techniques with all non-hydrogen atoms treated anisotropically. All calculations were performed on an Eclipse S/140 computer with the program package SHELXTL.

Solvent Extraction

The multitracer solution was prepared using $UO_2(NO_3)_2$ as the target material irradiated with a 60 MeV/nucleon $^{18}O^{8+}$ ion beam at the Heavy Ion Research Facility in Lanzhou, China. The chemical separation procedure was similar to the literature [12]. The obtained multitracer solution contained 12 radioactive rare earth nuclides: ^{140}La, ^{141}Ce, ^{147}Nd, ^{148}Pm, ^{147}Eu, ^{149}Gd, ^{153}Tb, ^{160}Er, ^{167}Tm, ^{166}Yb, ^{177}Lu and ^{87}Y. The solvents were saturated with each other prior to use to prevent volume changes of the phases during extraction. Ion strength was adjusted to be 0.1 with a lithium chloride solution. An aqueous picric acid solution (2.0 cm^3) containing the required multitracer at pH 2.50 was vigorously shaken with an equal volume of the nitrobenzene solution of L in a test tube with a ground stopper at room temperature for 5 min. After phase separation by centrifugation (1 min, 3000 rpm), 1.0-cm^3 samples were taken from each phase and their γ-activities were assayed using a calibrated HPGe γ-ray spectrometer. The detector had an efficiency of 40% and a resolution of 2.3 KeV at 1322 KeV. The γ-ray spectra recorded on 4096 channels were analysed and the peak areas of the spectra were computed with the code SAMPO [13] on a PII computer. Assignment of the nuclides to each peak of the γ-ray spectra was made on the basis of its energy and half-life. The distribution ratio (D) was determined as the ratio of the radioactivity of the organic and aqueous phases.

RESULTS AND DISCUSSION

Analytical data for the complexes conform to a 1 : 3 : 1 metal-to-picrate-to-L stoichiometry Ln(pic)$_3$L (see Table I). All complexes are soluble in $CHCl_3$, DMSO, DMF, CH_3CN, CH_3COCH_3, slightly soluble in C_2H_5OH, $CH_3COOC_2H_5$, and sparingly soluble in benzene, diethyl ether and cyclohexane.

IR spectra

The IR spectrum of free L shows bands at 1680 and 1111 cm^{-1} which may be assigned to ν(C=O) and ν(C–O–C), respectively. In the IR spectra of the lanthanum complex, the two bands shift by 70 and 33 cm^{-1} towards lower wave numbers, thus indicating that all the carbonyl and ether oxygen atoms take part in coordination to the metal ion. The larger shift for ν(C=O) in the spectra of the complexes suggests that the Ln–O (carbonyl) bond is stronger than Ln–O (ether).

The OH out-of-plane bending vibration of the free Hpic at 1151 cm^{-1} disappears in the spectra of the complexes, indicating that the H-atom of the OH group is replaced by Ln(III). The vibration ν(C–O) at 1265 cm^{-1} is shifted toward higher frequency by *ca.* 9 cm^{-1} in the complexes, suggesting that the interaction between metal ion and picrate group is very weak. The free Hpic has $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ at 1555 and 1342 cm^{-1}, while in the complexes they split into two bands at *ca.* 1576, 1540 cm^{-1} (for ν_{as}), and 1357, 1326 cm^{-1} (for ν_s), respectively. This indicates that some of the nitronyl oxygen atoms take part in coordination [14].

^{1}H NMR spectra

The spectrum of L exhibits three resolved signals at 7.41, 4.30 and 3.62 ppm assigned to phenothiazinyl, $–C(O)CH_2–$ and $–C_2H_4–$ protons, respectively. Upon coordination, the proton signals move to lower field. The signals of $–C(O)CH_2–$, $–C_2H_4–$ are shifted by 0.61 and 0.54 ppm, while those of the phenothiazinyl protons by only 0.09 ppm. This is due to the inductive effect of Ln–O (L) bonds. The fact that the shift is larger for

TABLE I Analytical data for the complexes

Complex	*Analysis* (%)[a]			
	C	*H*	*N*	*Ln*
La(Pic)$_3$L	33.85(33.67)	3.57(3.39)	10.16(9.82)	19.02(19.47)
Eu(pic)$_3$L	33.61(33.06)	3.80(3.33)	9.55(9.64)	20.15(20.92)
Y(pic)$_3$L	36.62(36.21)	3.98(3.65)	10.44(10.56)	13.32(13.40)

[a] Calculated values in parentheses.

–C(O)CH$_2$– protons than for –C$_2$H$_4$– ones indicates the Ln–O (C=O) bond is stronger than the Ln–O (C–O–C) one.

The proton signal of OH group in the free Hpic disappears in the complexes, indicating that the hydrogen atom of OH group is replaced by Ln(III). The benzene-ring protons of the free Hipc exhibit a *singlet* at 9.12 ppm. Upon coordination, the signal moves to a higher field. Only one *singlet* is observed for the benzene-ring protons of the three coordinated picrate, groups indicating fast exchange among the groups in solution [15].

Crystal Structure of the Erbium Complex

Figure 1 shows the structure and the atomic numbering scheme for the erbium complex. Figure 2 shows the molecular packing arrangement in the unit cell. A summary of the crystallographic data and details of the structure refinements are listed in Table II. Selected bond distances and angles are given in Table III.

The crystal structure is composed of [Er(pic)$_3$L] and one half C$_2$H$_5$OH molecule linked by weak *van der Waals* forces. The Er(III) ion is coordinated to nine oxygen atoms, five from L, four from two unidentate and one bidentate picrates. The coordination polyhedron is a tri-capped distorted trigonal prism. The ligand molecule wraps

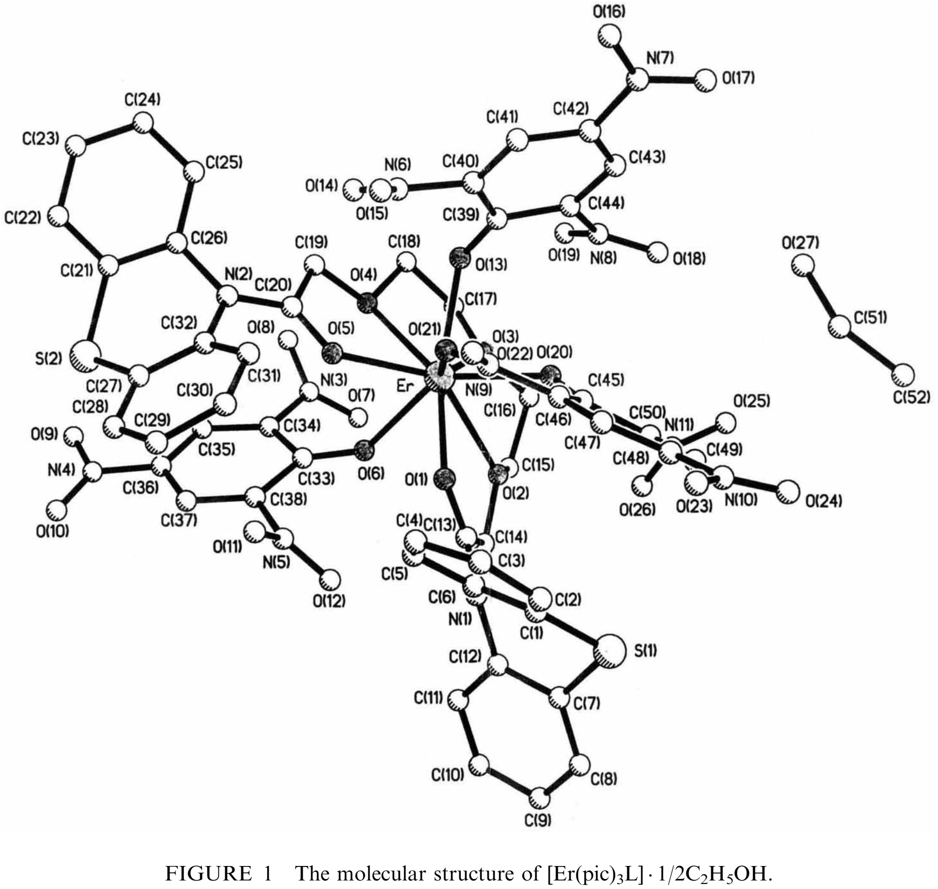

FIGURE 1 The molecular structure of [Er(pic)$_3$L] · 1/2C$_2$H$_5$OH.

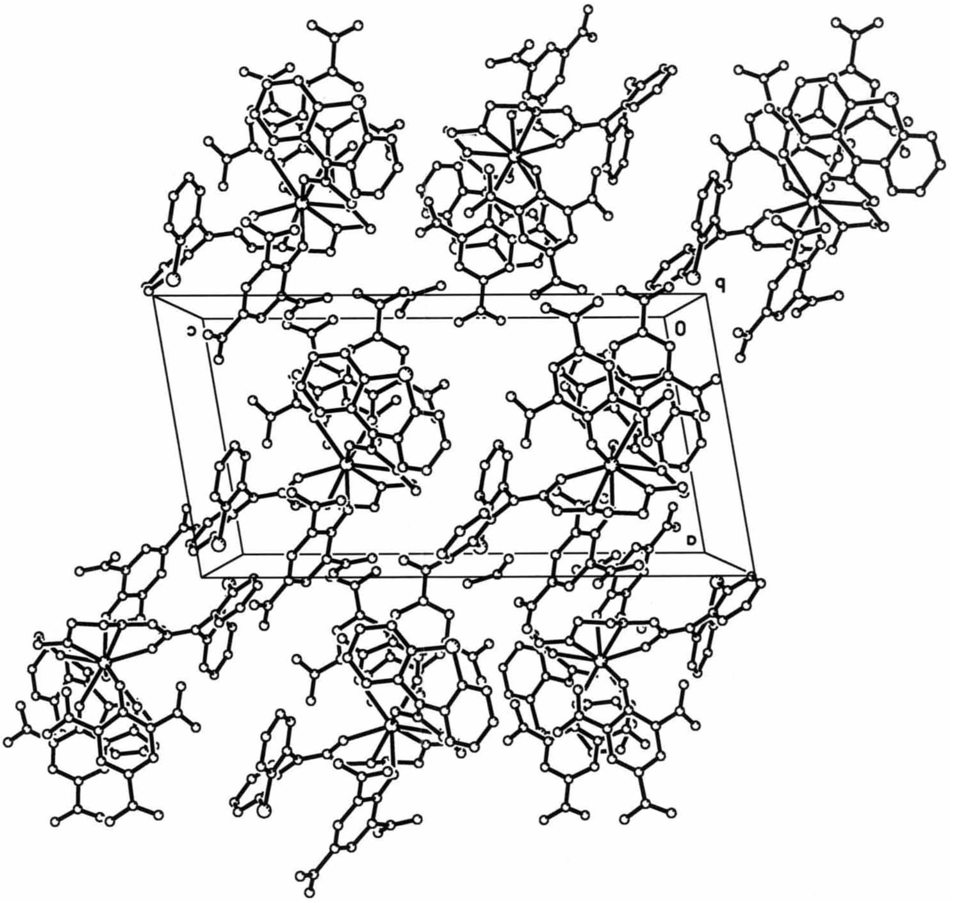

FIGURE 2 Unit cell contents for $[Er(pic)_3L] \cdot 1/2C_2H_5OH$.

around the metal ion with its oxygen atoms and forms a ring-like coordination structure together with one oxygen from the bidentate picrate at the open side of the ring (Fig. 3). Five oxygen atoms of L are almost coplanar, with a mean absolute deviation of 0.2047 Å from the mean plane. The erbium atom lies out of this plane by 0.5909 Å. Two other picrates are located outside the mean plane.

The average distance between the erbium and the coordination oxygen atoms is 2.372 Å. The Er–O (C=O) distance (mean 2.290 Å) is significantly shorter than the Er–O (C–O–C) one (mean 2.420 Å). This suggests that the Er–O (C=O) bond is stronger than the Er–O (C–O–C) one, in agreement with the IR spectrum data.

Extraction Studies

Extraction of ^{152}Eu(III) was carried out initially, in order to ascertain the optimum extraction condition. The effect of pH in aqueous phase on extraction behavior showed that extraction of ^{152}Eu(III) reached a maximum at pH 2.5. Thus, all other experiments were carried out at pH 2.5.

TABLE II Crystal data and structure refinement for the complex [Er(pic)$_3$L] · 1/2C$_2$H$_5$OH

Empirical formula	$C_{51}H_{37}N_{11}O_{26.50}S_2Er$
Temperature (K)	296(2)
Crystal color	Yellow
Crystal size (mm)	0.58 × 0.48 × 0.22
Formula weight	1459.30
Space group	$P2_1/c$
Crystal system	Monocliclic
Unit cell dimensions	
a (Å)	11.725(2)
b (Å)	21.569(3)
c (Å)	22.999(4)
β(°)	99.848(11)
V (Å^3)	5731(2)
Z	4
Density (calculated) (Mg m^{-3})	1.691
Absorption Coefficient (mm^{-1})	1.637
F (000)	2928
Radiation, graphite-monochromatized (Å)	0.71073
Reflections collected	9494
Independent reflections	9005
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.9918 and 0.7543
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9003/8/966
θ Range for data collection	1.76–24.00
Index range	$0 \leq h \leq 13$; $0 \leq k \leq 24$; $-26 \leq l \leq 25$
Goodness-of-fit on F^2	0.939
R [$I > 2\sigma(I)$][a]	$R_1 = 0.0355$, $wR_2 = 0.0831$
R (all data)	$R_1 = 0.0577$, $wR_2 = 0.0970$
Largest difference peak and hole [e Å^3]	0.859, −0.633

[a] $\omega = 1/[\sigma^2(F_O)^2 + (0.0337p)^2]$; $p = (F_O^2 + F_C^2)/3$.

TABLE III Selected bond lengths (Å) and angles (°) for [Er(pic)$_3$L] · 1/2C$_2$H$_5$OH

Er–O(1)	2.308(3)	Er–O(6)	2.374(3)
Er–O(2)	2.440(3)	Er–O(13)	2.309(3)
Er–O(3)	2.324(3)	Er–O(20)	2.274(3)
Er–O(4)	2.497(3)	Er–O(21)	2.551(4)
Er–O(5)	2.271(3)		
O(5)–Er–O(20)	136.36(12)	O(5)–Er–O(1)	89.03(12)
O(20)–Er–O(1)	76.94(13)	O(5)–Er–O(13)	83.96(12)
O(20)–Er–O(13)	76.56(13)	O(1)–Er–O(13)	132.64(12)
O(5)–Er–O(3)	128.91(12)	O(20)–Er–O(3)	88.23(13)
O(1)–Er–O(3)	132.17(12)	O(13)–Er–O(3)	85.17(13)
O(5)–Er–O(6)	73.11(12)	O(20)–Er–O(6)	140.24(13)
O(1)–Er–O(6)	78.19(11)	O(13)–Er–O(6)	141.70(12)
O(3)–Er–O(6)	85.98(12)	O(5)–Er–O(2)	137.14(12)
O(20)–Er–O(2)	72.51(12)	O(1)–Er–O(2)	64.60(11)
O(13)–Er–O(2)	138.84(12)	O(3)–Er–O(2)	67.58(12)
O(6)–Er–O(2)	68.93(12)	O(5)–Er–O(4)	64.27(11)
O(20)–Er–O(4)	137.91(12)	O(1)–Er–O(4)	145.07(11)
O(13)–Er–O(4)	69.58(11)	O(3)–Er–O(4)	65.13(12)
O(6)–Er–O(4)	72.88(11)	O(2)–Er–O(4)	119.94(11)
O(5)–Er–O(21)	69.11(12)	O(20)–Er–O(21)	67.43(13)
O(1)–Er–O(21)	65.82(12)	O(13)–Er–O(21)	67.96(12)
O(3)–Er–O(21)	146.82(12)	O(6)–Er–O(21)	127.18(12)
O(2)–Er–O(21)	121.28(11)	O(4)–Er–O(21)	118.64(11)

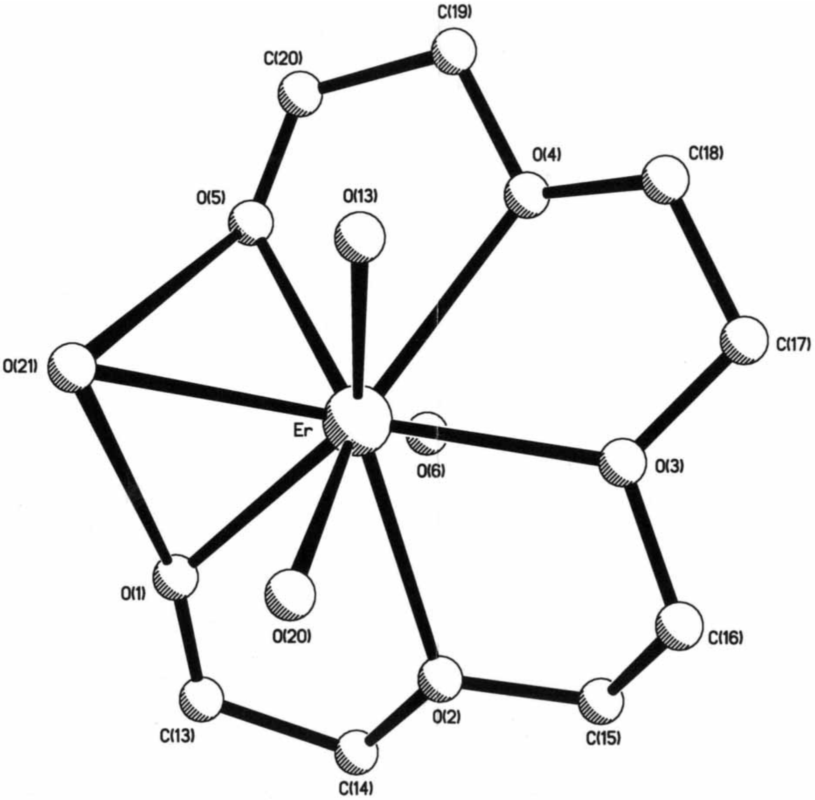

FIGURE 3 The ring-like coordination structure of $[Er(pic)_3L] \cdot 1/2C_2H_5OH$.

The L concentration variation (2.0×10^{-4} to 2.0×10^{-3} mol dm^{-1}) experiments were carried out under fixed aqueous phase conditions. The slope analysis result demonstrated that the stoichiometry of the extraction complex is $Eu(Pic)_3L$, this being in agreement with the result of the single cell analysis by X-ray.

In order to investigate the coordination selectivity of L for rare earth ions, the extraction of 12 rare earth elements by a nitrobenzene solution of L was carried out using the multitracer method. The percentage extractions of rare earth ions are plotted as a function of the reciprocal ionic radius (R^{-1}) of the rare earth in Fig. 4. It was observed that the extraction decreases regularly with increase in the atomic number. The percentage extraction of Y varies similarly with its ionic radius. The phenomenon of the reverse order has been reported in Refs. [16,17] where *N*,*N*,*N*′,*N*′-tetraphenyl-3,6-dioxaoctanediamide [16] and 18-crown-6 [17] were used for extraction of rare earth elements, respectively. The reverse extraction sequence suggests that extractabilities of trivalent rare earth cations are determined mainly by the hydration energy of the cations extracted. The extraction of the heavier rare earth ions, possessing higher hydration free energy, is more difficult than that of the lighter rare earth ions, possessing lower hydration free energy. Similarly, in studies on the extraction of alkaline earth metal picrates, the barium ion, with the lowest hydration energy in the series, is favored over any other alkaline earths, irrespective of the cavity size

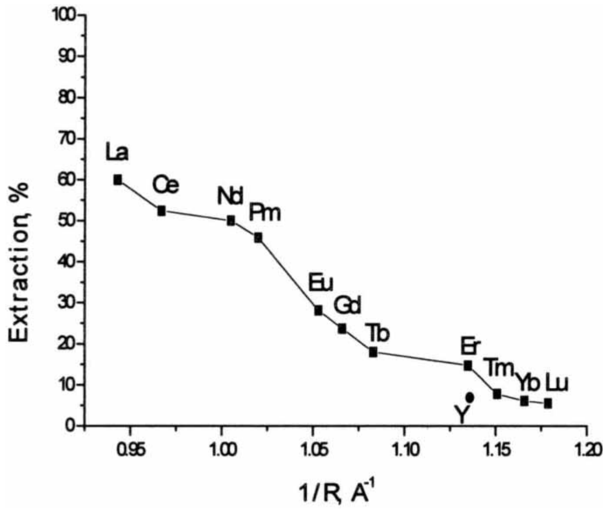

FIGURE 4 Percentage extraction as a function of the reciprocal ionic radius of the rare earth.

TABLE IV Extraction selectivity of L for the rare earth ions

	La	*Ce*	*Nd*	*Pm*	*Eu*	*Gd*	*Tb*	*Er*	*Tm*	*Yb*	*Lu*	*Y*
D	1.5	1.1	1	0.85	0.39	0.31	0.25	0.2	0.09	0.065	0.058	0.074
$SF_{La/Ln}$	1	1.4	1.5	1.8	3.8	4.8	6	7.5	17.6	23.1	25.9	20.3

of the ligand [18]. It seems that the reverse order is a common characteristic when crown-ethers, either cyclic or acyclic, are employed as extractants. This is ascribed to the weaker ability of C=O to coordinate to a metal cation than P=O to do so. The crown ether, unlike TBP, cannot completely replace the hydration water molecules bound tightly in the first solvation shell of the cations.

The extraction selectivities of L for the rare earth elements are listed in Table IV. It can be seen that inter-group separation of the rare earth elements by L is possible, although inner-group separation factors are not high.

CONCLUSION

The structural results above show that L acts as a pentadentate ligand forming a ring-like coordinate structure. The internal cavity formed by the coordinating oxygen atoms is suitable for the uptake of a cation. The reverse extraction sequence suggests that L is a useful extractant in the separation between lighter and heavier rare earth elements. Further studies on other open-chain crown ethers with different structures (the length of $–CH_2OCH_2–$ units and terminal groups) as extractants must be of significance both in the study of coordination chemistry and in the predetermined design and synthesis of new extractants for rare earth elements.

TABLE V Coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms

	x	y	z	U_{eq}
Er	3933(1)	924(1)	7813(1)	29(1)
S(1)	7264(1)	3089(1)	9285(1)	57(1)
S(2)	926(1)	1786(1)	5126(1)	55(1)
O(1)	4647(3)	1919(2)	7969(2)	35(1)
O(2)	3701(3)	1391(2)	8752(2)	37(1)
O(3)	3046(3)	258(2)	8393(2)	41(1)
O(4)	2350(3)	274(2)	7258(2)	33(1)
O(5)	3415(3)	1150(2)	6839(2)	34(1)
O(6)	2204(3)	1517(2)	7714(2)	37(1)
O(7)	314(4)	826(2)	7993(2)	63(1)
O(8)	−299(4)	357(2)	7163(2)	74(1)
O(9)	−2104(4)	1913(3)	5744(2)	98(2)
O(10)	−1229(5)	2777(3)	5690(3)	113(2)
O(11)	2923(4)	2839(2)	6769(2)	78(1)
O(12)	2627(4)	2846(2)	7666(2)	64(1)
O(13)	4685(3)	33(2)	7470(2)	39(1)
O(14)	4728(4)	69(2)	6272(2)	71(1)
O(15)	6395(4)	422(2)	6156(2)	74(1)
O(16)	9430(4)	−1003(2)	7014(3)	75(1)
O(17)	9629(4)	−1147(2)	7955(3)	89(2)
O(18)	6416(5)	−624(3)	8962(3)	110(2)
O(19)	4774(4)	−765(2)	8425(2)	86(2)
O(20)	5618(3)	781(2)	8453(2)	44(1)
O(21)	5712(3)	1147(2)	7345(2)	44(1)
O(22)	7341(5)	1470(3)	7172(3)	109(2)
O(23)	10346(6)	2186(3)	8634(5)	143(4)
O(24)	10430(6)	1834(3)	9509(4)	170(4)
O(25)	6988(13)	605(6)	9975(5)	338(10)
O(26)	5677(7)	1225(5)	9704(3)	180(4)
N(l)	5091(3)	2798(2)	8483(2)	36(1)
N(2)	2658(3)	1013(2)	5888(2)	36(1)
N(3)	109(4)	807(2)	7455(3)	48(1)
N(4)	−1312(5)	2276(3)	5907(3)	73(2)
N(5)	2402(4)	2672(2)	7157(3)	48(1)
N(6)	5769(4)	134(2)	6438(2)	50(1)
N(7)	9081(4)	−965(2)	7486(3)	58(2)
N(8)	5790(5)	−634(3)	8484(3)	66(2)
N(9)	6711(4)	1313(2)	7513(2)	56(1)
N(10)	9950(6)	1909(4)	9014(6)	l18(4)
N(11)	6557(7)	981(4)	9617(3)	104(2)
C(1)	7102(4)	3071(2)	8506(3)	44(1)
C(2)	8041(5)	3164(3)	8226(4)	56(2)
C(3)	7920(6)	3126(3)	7623(4)	62(2)
C(4)	6853(6)	3019(3)	7293(3)	60(2)
C(5)	5893(5)	2926(3)	7560(3)	50(2)
C(6)	6023(4)	2932(2)	8165(3)	39(1)
C(7)	5887(4)	3396(2)	9348(2)	40(1)
C(8)	5752(5)	3813(3)	9787(3)	47(2)
C(9)	4684(5)	4068(3)	9811(3)	49(2)
C(10)	3755(5)	3915(3)	9383(3)	46(2)
C(11)	3866(5)	3490(3)	8948(3)	41(1)
C(12)	4922(4)	3228(2)	8940(2)	36(1)
C(13)	4507(4)	2259(2)	8386(2)	33(1)
C(14)	3725(5)	2052(3)	8807(3)	39(1)
C(15)	2907(6)	1081(3)	9072(3)	48(2)
C(16)	3129(7)	402(3)	9008(3)	53(2)
C(17)	2223(5)	−219(3)	8173(3)	43(2)
C(18)	2280(5)	−325(3)	7537(3)	43(2)

(*continued*)

TABLE V Continued

C(19)	2321(5)	226(3)	6639(3)	39(1)
C(20)	2833(4)	826(2)	6455(2)	33(1)
C(21)	1179(4)	998(3)	5007(2)	41(1)
C(22)	598(5)	698(4)	4509(3)	56(2)
C(23)	811(5)	89(4)	4410(3)	61(2)
C(24)	1634(5)	−237(3)	4802(3)	55(2)
C(25)	2243(5)	61(3)	5295(3)	45(2)
C(26)	2009(4)	670(3)	5401(2)	38(1)
C(27)	2377(5)	2007(3)	5408(2)	43(1)
C(28)	2769(6)	2594(3)	5283(3)	56(2)
C(29)	3901(6)	2755(3)	5484(3)	60(2)
C(30)	4660(6)	2333(3)	5799(3)	51(2)
C(31)	4262(5)	1755(3)	5927(3)	45(1)
C(32)	3122(4)	1606(2)	5748(2)	37(1)
C(33)	1379(4)	1702(2)	7325(2)	35(1)
C(34)	326(4)	1367(2)	7132(2)	39(1)
C(35)	−512(5)	1535(3)	6665(3)	47(2)
C(36)	−404(5)	2078(3)	6378(3)	48(2)
C(37)	557(5)	2440(3)	6538(3)	47(2)
C(38)	1406(4)	2260(2)	6991(2)	38(1)
C(39)	5662(4)	−209(2)	7467(3)	41(1)
C(40)	6288(4)	−169(2)	6982(3)	40(1)
C(41)	7387(5)	−398(3)	6998(3)	43(2)
C(42)	7945(4)	−695(3)	7498(3)	46(2)
C(43)	7429(5)	−750(3)	7983(4)	51(2)
C(44)	6320(5)	−525(3)	7966(3)	47(2)
C(45)	6563(5)	1075(3)	8563(3)	47(2)
C(46)	7175(4)	1332(3)	8137(3)	47(2)
C(47)	8261(5)	1612(3)	8285(4)	67(2)
C(48)	8764(6)	1645(3)	8860(5)	82(3)
C(49)	8229(7)	1437(4)	9308(5)	81(3)
C(50)	7146(6)	1168(3)	9158(3)	64(2)
O(27)	9779(22)	−214(14)	9342(11)	229(10)
C(51)	10430(20)	295(12)	9619(18)	183(15)
C(52)	10804(24)	449(17)	10247(16)	189(16)

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