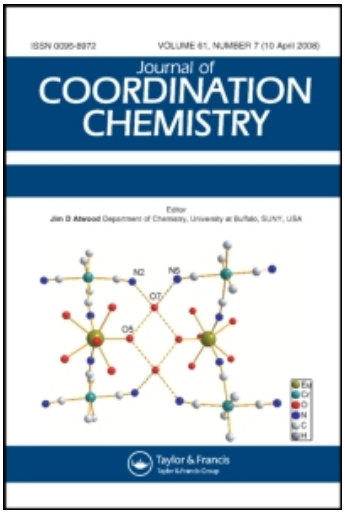

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SYNTHESIS, CHARACTERIZATION AND STRUCTURE OF COMPLEXES OF LANTHANUM(III) PICRATE WITH *N, N, N′, N′*-TETRAPHENYL-3, 6, 9-TRIOXAUNDECANEDIAMIDE

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SYNTHESIS, CHARACTERIZATION AND STRUCTURE OF COMPLEXES OF LANTHANUM(III) PICRATE WITH *N, N, N′, N′*-TETRAPHENYL-3, 6, 9-TRIOXAUNDECANEDIAMIDE

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Reaction of lanthanum picrate with *N, N, N′, N′*-tetraphenyl-3, 6, 9-trioxaundecanediamide (TTD) yields [La $(Pic)_3$ (TTD)], which has been characterized by elemental analysis, IR and ^1H NMR spectra and molar conductivity measurements. The complex crystallizes in the orthorhombic space group *Pcab* with $a = 24.006(8)$, $b = 29.140(9)$, $c = 32.084(9)$ Å and $D_c = 1.60$g cm^{-3} for $Z = 16$. Refinement of 5676 reflections ($I \geq 2.0\sigma(I)$) out of 12569 unique observed reflections ($2° \leq 2\theta \leq 42°$) gave R and R_w values of 0.079 and 0.068, respectively.

Keywords: Lanthanum picrate; TTD; complex; X-ray structure

INTRODUCTION

Noncyclic polyethers offer many advantages over the use of crown ethers in the extraction and analysis (ion- selective electrodes) of the rare earths.[1–5] The extraction of fission products by *N, N, N′, N′*-tetrapenyl-3, 6, 9-trioxaundecanediamide (TTD) has been studied by an isotopic tracer technique and the extractability of alkaline earths and rare earths by nitrobenzene solution of TTD is very high (99.05% for La(III), 98.89% for Ce(III), 94.76% for Nd(III)), when picrate is used as an accompanying ion.[5] In addition, TTD was

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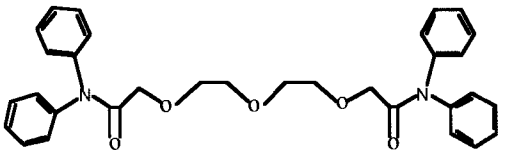
used as the active material for a barium ion selective electrode,[6] showing excellent e. m. f. stability (drift less than 0.8mV/day) and an operational lifetime of more than two years in contrast to earlier systems.[7] The sensor discriminates against alkali and alkaline earth metal cations by factors of approximately $10^2 - 10^3$ and $30 - 10^5$, respectively. In order to further investigate the relation between structure and properties and to find a more promising extractant, we report here the synthesis and crystal structure of the La(III) picrate complex with TTD.



N, N, N′, N′-tetraphenyl-3, 6, 9-trioxaundecanediamide (TTD).

EXPERIMENTAL

Reagents

Lanthanum(III) picrate[8] and TTD[9–10] were prepared according to literature methods. All solvents used were purified by standard methods.

Chemical and physical measurements

Lanthanum(III) ion was determined by EDTA titration using xylenol orange as indicator. Carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyser. Conductivity measurement was carried out with a DDS-11A conductivity bridge using a 10^{-3} mol dm^{-3} solution in CH_3CN at 25°C. IR spectra were recorded on a Nicolet 170SX FT-IR instrument using KBr discs in the 4000 — 220 cm^{-1} region. ^1H NMR spectra were measured on an FT-80A spectrometer in $CDCl_3$ solutions with TMS as internal standard.

Synthesis of [La(Pic)$_3$(TTD)]

A solution of 0.1 mmol TTD in 15 cm^3 of anhydrous ethanol was added dropwise to a solution of 0.1 mmol lanthanum(III) picrate 20 cm^3 of anhydrous

ethanol. The mixture was stirred at room temperature for 2 h. The precipitated solid complex was filtered, washed with anhydrous ethanol and dried *in vacuo* over P_4O_{10} for 48 h. *Anal.; calcd.* for [La(Pic)$_3$(TTD)]: C, 44.55; H, 2.84; N, 11.43; La, 10.30%. *Found*: C, 44.68; H, 2.64; N, 11.14; La, 10.71%. The solid complex was recrystallized from MeCN by slow evaporation to obtain transparent yellow crystals of [La(Pic)$_3$(TTD)].

X-ray structure determination for [La(Pic)$_3$(TTD)]

Crystal data: $C_{50}H_{38}N_{11}LaO_{26}$, $M_r = 1347.8$, orthorhombic, space group *Pcab*, $a = 24.006(8)$, $b = 29.140(9)$, $c = 32.084(9)$ Å, $U = 22444(12)$ Å^3, $Z = 16$, $D_c = 1.60$g cm^{-3}, λ(Mo*K*α) = 0.7107 Å, $F(000) = 10880$, μ(Mo*K*α) = 8.80 cm^{-1}. Intensity data for a crystal $0.40 \times 0.40 \times 0.60$ mm were measured at 21°C on an R3M/E four-circle diffractometer with graphite monochromatized Mo*K*α radiation, using a $\omega/2\theta$ scan. Lorentz and polarization corrections were applied, but no absorption correction was made.

The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by block-matrix least-squares procedures based on F. Non-hydrogen atoms were refined anisotropically. The weight scheme was $w = [\sigma^2(F) + 0.00010F^2]^{-1}$ $\{1\text{-exp}[-5(\sin\theta/\lambda)^2]\}$, final $R_w = 0.068$, $R = 0.079$. The highest peak in the final difference Fourier was 0.74 e Å^{-3}. All calculations were performed on an Eclipse/S 140 computer with the SHELXTL program. Final atomic coordinates are given in Table I. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structures are available as supplementary data from W.L., upon request.

TABLE I Final fractional atomic coordinates ($\times 10^4$, for La $\times 10^5$) with e.s.d.'s in parentheses for non–H atoms and *Ueq* ($\times 10^4$)

Atom	*x/a*	*y/b*	*z/c*	*Ueq(Å^2)*	*Atom*	*x/a*	*y/b*	*z/c*	*Ueq(Å^2)*
La1	80502(4)	30835(3)	25067(4)	42.2(3)	N12	1155(5)	4490(5)	6215(4)	60(5)
La2	21818(4)	52127(3)	52160(3)	44.4(3)	N13	3782(5)	4981(5)	4421(4)	53(5)
N1	9522(4)	2462(5)	3280(4)	37(4)	N14	2204(6)	5533(5)	6532(4)	71(5)
N2	6435(5)	2665(4)	1781(4)	48(5)	N15	3983(7)	5046(6)	7118(5)	98(6)
N3	9754(5)	3226(5)	2028(5)	62(5)	N16	3896(7)	5465(6)	5641(5)	84(6)
N4	10016(7)	2934(7)	548(6)	118(7)	N17	1900(8)	5260(7)	3874(10)	168(7)
N5	8144(7)	3007(6)	1092(4)	82(5)	N18	458(8)	4159(7)	3447(6)	124(7)
N6	6168(6)	3459(5)	2915(5)	72(5)	N19	626(7)	4614(7)	4870(5)	147(7)
N7	6109(6)	3214(6)	4416(5)	86(6)	N20	1641(7)	3712(5)	4512(6)	117(6)
N8	7881(6)	3119(5)	3688(4)	63(5)	N21	3000(8)	2649(4)	5104(7)	129(7)
N9	7255(6)	1931(5)	3475(4)	80(5)	N22	3065(5)	4247(4)	5566(4)	61(5)
N10	8209(9)	537(5)	3002(7)	140(7)	O27	1815(4)	4833(4)	5842(3)	54(4)

TABLE I *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	*Ueq(Å²)*	*Atom*	*x/a*	*y/b*	*z/c*	*Ueq(Å²)*
N11	8446(5)	1948(5)	2228(4)	55(5)	O28	1284(4)	5533(3)	5638(4)	55(4)
O1	8882(4)	2618(4)	2780(3)	45(4)	O29	1810(4)	6082(4)	5128(4)	74(5)
O2	8970(4)	3477(3)	2823(4)	50(4)	O30	2738(4)	5783(3)	4733(4)	62(4)
O3	8166(4)	4004(4)	2475(4)	61(4)	O31	3023(4)	4973(4)	4828(4)	68(4)
O4	7332(4)	3596(4)	2058(3)	50(4)	O32	2727(4)	5603(4)	5737(3)	62(4)
O5	7255(5)	2730(3)	2110(4)	61(4)	O33	1963(5)	5260(5)	6759(4)	86(5)
O6	8600(4)	3231(4)	1905(3)	52(4)	O34	1999(5)	5860(4)	6361(4)	85(5)
O7	9842(6)	2907(4)	2245(4)	92(5)	O35	3712(7)	5016(6)	7447(5)	124(6)
O8	9821(5)	3621(5)	2131(4)	87(5)	O36	4477(7)	5015(6)	7070(5)	134(6)
O9	10507(8)	3077(7)	612(6)	141(7)	O37	4285(7)	5229(8)	5567(6)	155(7)
O10	9844(8)	2742(8)	242(6)	165(7)	O38	3761(7)	5744(7)	5404(5)	133(6)
O11	7969(7)	2773(5)	809(5)	116(6)	O39	1545(5)	5238(5)	4670(4)	87(5)
O12	7813(6)	3216(8)	1299(5)	163(6)	O40	2398(9)	5141(8)	3932(10)	229(8)
O13	7283(4)	3369(4)	2918(4)	68(4)	O41	1867(10)	5639(8)	3811(7)	204(8)
O14	6101(6)	3850(5)	2801(5)	107(6)	O42	721(10)	4138(7)	3119(7)	185(7)
O15	6033(5)	3143(5)	2706(5)	95(5)	O43	53(8)	4001(7)	3555(6)	154(7)
O16	5621(5)	3318(6)	4409(5)	110(6)	O44	163(8)	4477(8)	4925(7)	177(7)
O17	6353(5)	3099(6)	4729(5)	113(6)	O45	897(6)	4737(6)	5186(5)	122(6)
O18	8086(5)	3060(6)	4035(4)	96(5)	O46	2117(4)	4419(3)	5027(3)	54(4)
O19	8165(4)	3127(4)	3363(3)	64(4)	O47	1798(9)	3885(7)	4218(4)	190(7)
O20	7744(5)	2387(3)	2848(4)	58(4)	O48	1246(8)	3700(7)	4713(9)	192(7)
O21	6815(7)	2061(8)	3366(6)	158(7)	O49	2798(8)	2386(5)	4890(6)	153(6)
O22	7395(9)	1992(7)	3822(5)	149(7)	O50	3371(7)	2573(5)	5373(6)	118(6)
O23	7992(10)	342(5)	3278(7)	186(7)	O51	3491(7)	4137(5)	5768(6)	121(6)
O24	8476(10)	361(5)	2728(7)	176(7)	O52	2899(4)	4639(3)	5610(3)	55(4)
O25	8817(5)	1720(4)	2045(4)	74(5)	C51	1482(7)	4089(6)	6244(6)	59(6)
O26	8292(5)	2321(3)	2111(4)	64(4)	C52	1913(8)	4063(7)	6542(7)	76(6)
C1	9680(7)	1839(7)	2807(6)	67(6)	C53	2240(8)	3639(7)	6537(6)	77(6)
C2	9737(7)	1368(7)	2719(6)	60(6)	C54	2114(8)	3294(7)	6254(7)	89(7)
C3	9665(9)	1042(7)	3047(7)	83(7)	C55	1696(8)	3334(7)	5978(8)	92(7)
C4	9538(9)	1190(7)	3452(7)	94(7)	C56	1375(9)	3726(8)	5961(7)	92(7)
C5	9488(8)	1676(6)	3522(6)	63(6)	C57	615(7)	4519(5)	6431(6)	50(6)
C6	9549(6)	1977(5)	3194(5)	40(5)	C58	148(7)	4327(7)	6224(7)	76(6)
C7	9826(6)	2620(5)	3653(5)	40(5)	C59	−366(8)	4326(8)	6455(5)	115(7)
C8	9500(8)	2684(6)	3999(5)	68(6)	C60	−378(10)	4502(8)	6850(5)	130(8)
C9	9804(9)	2831(7)	4376(6)	76(6)	C61	96(9)	4689(9)	7041(8)	125(8)
C10	10378(8)	2921(7)	4364(7)	85(7)	C62	607(9)	4700(8)	6827(6)	95(7)
C11	10673(8)	2966(7)	3982(6)	77(6)	C63	1345(7)	4855(5)	5997(5)	50(5)
C12	10394(7)	2710(6)	3613(7)	67(6)	C64	999(7)	5276(6)	5969(6)	62(6)
C13	9209(6)	2737(5)	3045(5)	43(5)	C65	1091(8)	5995(7)	5620(7)	75(6)
C14	9318(7)	3259(5)	3132(5)	51(5)	C66	1238(7)	6186(7)	5217(8)	94(7)
C15	9007(7)	3980(5)	2856(5)	53(6)	C67	1975(10)	6314(7)	4743(7)	100(7)
C16	8750(6)	4179(5)	2487(7)	54(5)	C68	2617(7)	6286(5)	4719(7)	77(6)

TABLE I *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	*Ueq(Å²)*	*Atom*	*x/a*	*y/b*	*z/c*	*Ueq(Å²)*
C17	7873(8)	4255(6)	2150(6)	82(6)	C69	3251(7)	5693(6)	4517(7)	68(6)
C18	7277(7)	4088(6)	2152(5)	58(6)	C70	3360(7)	5192(7)	4590(5)	65(6)
C19	6826(7)	3439(4)	1855(6)	56(6)	C71	4201(7)	5248(7)	4188(6)	66(6)
C20	6867(6)	2910(4)	1934(4)	47(5)	C72	4594(9)	5507(8)	4419(8)	97(7)
C21	5992(7)	2863(6)	1523(6)	60(6)	C73	4991(9)	5737(7)	4157(8)	92(7)
C22	6116(8)	2939(7)	1115(6)	78(6)	C74	4999(9)	5698(8)	3748(7)	99(7)
C23	6661(9)	3107(9)	867(7)	97(7)	C75	4623(10)	5441(8)	3524(8)	106(7)
C24	5120(7)	3168(7)	1045(7)	83(7)	C76	4192(8)	5207(8)	3761(6)	79(6)
C25	5031(9)	3102(8)	1458(6)	87(7)	C77	3881(7)	4486(7)	4461(7)	73(6)
C26	5479(8)	2929(6)	1726(6)	66(6)	C78	4382(8)	4357(7)	4651(7)	85(7)
C27	6392(7)	2191(6)	1898(7)	69(6)	C79	4447(9)	3863(9)	4711(7)	106(7)
C28	6342(8)	1867(8)	1583(7)	84(7)	C80	4059(12)	3560(9)	4559(8)	111(8)
C29	6276(8)	1390(8)	1681(7)	92(7)	C81	3575(11)	3715(7)	4351(8)	96(7)
C30	6244(8)	1271(7)	2096(6)	96(7)	C82	3466(8)	4189(7)	4308(6)	80(6)
C31	6296(9)	1581(7)	2414(7)	120(7)	C83	3012(7)	5502(5)	6056(5)	53(5)
C32	6369(8)	2054(7)	2318(7)	88(7)	C84	2798(7)	5427(6)	6455(5)	55(6)
C33	8907(8)	3154(6)	1587(5)	53(6)	C85	3074(9)	5290(6)	6813(6)	70(6)
C34	9514(8)	3158(7)	1615(5)	63(6)	C86	3663(9)	5199(7)	6749(7)	77(7)
C35	9869(9)	3086(7)	1292(6)	79(6)	C87	3927(8)	5271(7)	6373(7)	72(6)
C36	9640(8)	2991(8)	903(5)	83(6)	C88	3611(7)	5410(6)	6042(6)	59(6)
C37	9085(7)	2951(7)	842(5)	65(6)	C89	1309(8)	4977(7)	4409(7)	74(6)
C38	8725(7)	3050(7)	1182(6)	70(6)	C90	1447(7)	4964(6)	4000(6)	72(6)
C39	7039(6)	3325(5)	3272(5)	53(5)	C91	1241(10)	4728(8)	3659(7)	94(7)
C40	6448(6)	3397(6)	3322(5)	55(6)	C92	764(9)	4448(7)	3779(6)	90(7)
C41	6123(6)	3336(6)	3661(5)	52(5)	C93	551(8)	4427(7)	4166(6)	79(6)
C42	6421(8)	3254(6)	4022(5)	61(6)	C94	811(7)	4693(8)	4448(4)	83(6)
C43	6988(7)	3171(7)	4031(6)	67(6)	C95	2341(6)	4022(5)	5073(5)	51(6)
C44	7278(7)	3212(6)	3657(6)	59(6)	C96	2145(8)	3653(6)	4841(6)	68(6)
C45	7828(6)	1966(5)	2857(4)	43(5)	C97	2318(7)	3199(6)	4831(7)	82(6)
C46	7622(7)	1702(6)	3175(5)	63(6)	C98	2765(8)	3125(5)	5113(6)	74(6)
C47	7684(10)	1245(6)	3232(7)	91(7)	C99	3022(7)	3450(6)	5346(6)	67(6)
C48	8062(10)	1020(4)	2948(7)	103(7)	C100	2802(6)	3904(5)	5323(4)	46(5)
C49	8312(8)	1262(5)	2627(7)	82(6)					
C50	8189(6)	1707(5)	2579(5)	52(5)					

RESULTS AND DISCUSSION

Analytical data indicate that the complex has a 1:3:1 metal:picrate:TTD stoichiometry. It is soluble in DMSO, acetone, chloroform and acetonitrile, slightly soluble in methanol and ethyl acetate and sparingly soluble in benzene, ether and cyclohexane. The molar conductance of the complex in CH_3CN is 23.4 S cm^2

mol^{-1}, which indicates that is a non-electrolyte,[11] implying that all the picrate groups are in the coordination sphere.

IR spectra

The IR spectrum of free TTD shows bands at 1686 and 1140 cm^{-1} which may be assigned to ν(C ═O) and ν_{as} (C—O—C), respectively. In the complex, the two bands shift by *ca* 74 and 62 cm^{-1}, respectively, towards lower wavenumbers thus indicating that all the ether oxygen atoms and the C═O groups take part in coordination to La(III). The larger shift for ν(C═O) in the spectrum of the complex suggests that the La—O (carbonyl) bond is stronger than La—O(ether). These results are consistent with the molar conductance value and the crystal structure determination.

The OH out-of-plane bending vibration of free Hpic at 1151 cm^{-1} disappears in the spectrum of the complex, indicating that the hydrogen atom of the OH group is replaced by La(III). The ν(C—O) vibration at 1265cm^{-1} is shifted towards higher frequency by *ca* 10 cm^{-1} in the complex. This is due to the following two effects. First, the hydrogen atom of OH group is replaced by La(III), increasing π- bond character in the C—O bond. Secondly, coordination of oxygen atom of TTD to La(III) causes the π- character to be weakened. This suggests that the interaction between metal ion and picrate groups is very weak. Free Hpic has ν_{as}(—NO_2) and ν_s(—NO_2) at 1555 and 1342 cm^{-1}, respectively, which split into two bands at *ca* 1576, 1538 and 1360, 1328 cm^{-1}, respectively, in the complex. This indicates that some of the nitro group oxygen atoms take part in coordination.[8]

^{1}H NMR spectra

The spectrum of TTD exhibits three proton signals at 7.34, 4.07 and 3.68 ppm, assigned to —C_6H_5, —$C(O)CH_2$— and—C_2H_4 — protons, respectively. Upon coordination, all the ligand proton signals move to lower field, among which —$C(O)CH_2$— and— C_2H_4— protons shift by some 0.5 and 0.2 ppm, respectively, while C_6H_5 — protons shift 0.1 ppm. This is due to the inductive effect of La(III) in the complex and is in agreement with IR spectra.

The proton signal of the OH group in free Hpic disappears in the complex, again indicating that the hydrogen atom of OH group is replaced by La(III). Benzene ring protons of free Hpic give a singlet at 9.12 ppm. Upon coordination, the signal shifts towards higher field by *ca* 0.6 ppm. This is due to the replacement of the proton by La(III) and to increased screening effects.

Crystal Structure of the lanthanum complex

The structure of $[La(Pic)_3(TTD)]$ is shown in Figure 1 and selected bonding parameters are given in Table II. Figure 2 shows the molecular packing arrangement in the unit cell. The crystal structure is composed of discrete molecular units linked by weak van der Waals forces. In one asymmetric unit there are two independent $[La(Pic)_3(TTD)]$ monomers, designated $[La1(Pic)_3(TTD)]$ and $[La2(Pic)_3(TTD)]$, the structures of which are different. The La1 ion is 10-coordinated by five oxygen atoms of TTD and five oxygen atoms of one unidentate and two bidentate picrates, while the La2 ion is 9-coordinated by five oxygen atoms of TTD and four oxygen atoms of one bidentate and two unidentate picrates. The La1 — O lengths are longer than the corresponding La2—O bonds (Table II), suggesting that the La2 ion lies nearer to the coordinated oxygen atoms than the La1 ion.

TABLE II Selected bond lengths (Å) and angles (deg) in the La1 and La2 monomers

La1—O1	2.569(10)	La2—O27	2.456(11)
La1—O2	2.687(10)	La2—O28	2.712(11)
La1—O3	2.698(10)	La2—O29	2.701(11)
La1—O4	2.697(10)	La2—O30	2.636(11)
La1—O5	2.515(11)	La2—O31	2.473(11)
La1—O6	2.376(10)	La2—O32	2.408(11)
La1—O13	2.415(11)	La2—O39	2.327(12)
La—O19	2.763(11)	La2—O46	2.398(11)
La1—020	2.422(10)	La2—O52	2.714(11)
La1—O26	2.622(11)		
Mean lengths			
La1—O(C—O, Pic)	2.404	La2—O(C—O, Pic)	2.378
La1—O(C=O, TTD)	2.542	La2—O(C=O, TTD)	2.464
La1—O(C—O—C, TTD)	2.694	La2—O(C—O—C, TTD)	2.683
La1—O(NO_2, Pic)	2.692	La2—O(NO_2, Pic)	2.714
O1—La1—O2	57.2(3)	O27—La2—O28	57.4(3)
O1—La1—O6	86.6(3)	O27—La2—O32	80.8(4)
O1—La1—O19	66.9(3)	O27—La2—O46	75.3(4)
O1—La1—O20	68.8(3)	O27—La2—O52	64.4(3)
O1—La1—O26	63.0(3)	O28—La2—O29	57.8(3)
O2—La1—O3	60.4(3)	O28—La2—O32	85.6(3)
O2—La1—O6	76.9(3)	O28—La2—O39	80.9(4)
O2—La1—O19	61.5(3)	O29—La2—O30	61.0(3)
O3—La1—O4	59.7(3)	O29—La2—O32	79.1(4)
O3—La1—O6	74.5(4)	O29—La2—O39	71.0(4)
O3—La1—O13	75.9(4)	O30—La2—O31	57.9(3)
O3—La1—O19	89.0(4)	O30—La2—O32	80.5(4)
O4—La1—O5	58.1(3)	O30—La2—O39	82.6(4)
O4—La1—O6	79.7(3)	O31—La2—O32	92.2(4)

TABLE II *(Continued)*

O4—La1—O13	67.2(4)	O31—La2—O39	99.6(4)
O5—La1—O6	94.9(4)	O31—La2—O46	69.7(3)
O5—La1—O13	80.7(4)	O31—La2—O52	62.7(3)
O5—La1—O20	69.8(4)	O32—La2—O52	68.1(4)
O5—La1—O26	64.9(3)	O39—La2—O46	78.4(4)
O6—La1—O26	68.8(4)	O46—La2—O52	63.7(3)
O20—La1—O26	64.9(4)		

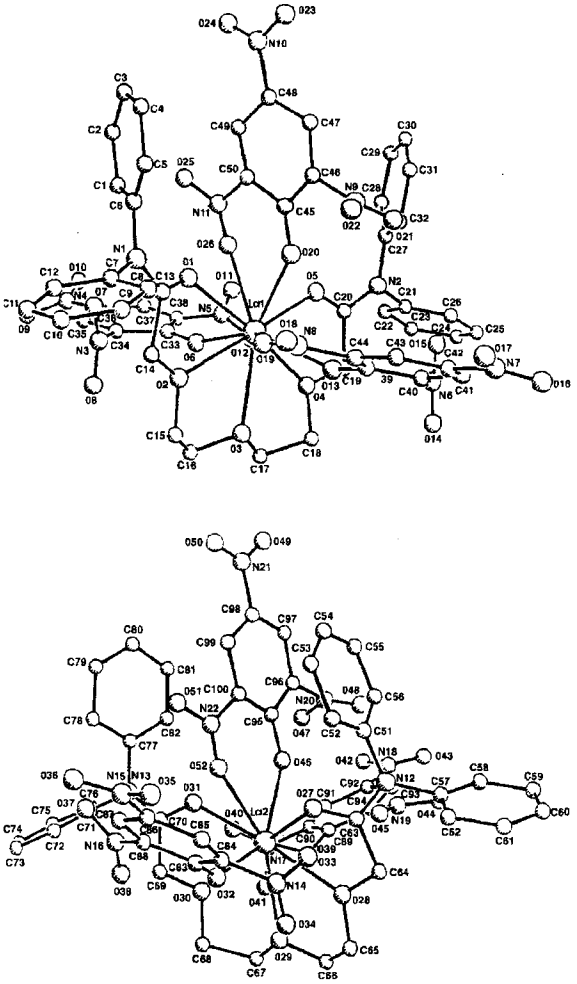


FIGURE 1 The structures of the two independent monomers, designated La1 and La2, (above and below, respectively), in the asymmetric unit of $[La(Pic)_3(TTD)]$.

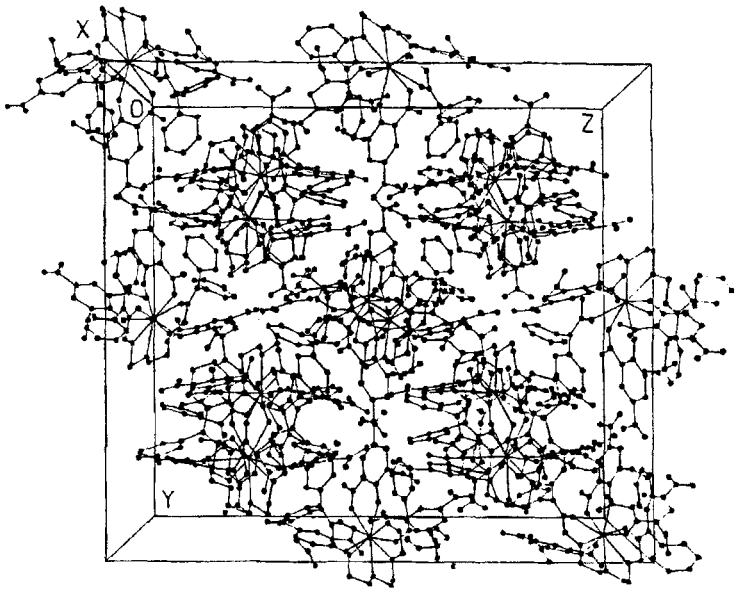


FIGURE 2 Unit cell contents for $[La(Pic)_3(TTD)]$.

The five oxygen atoms of TTD are not quite coplanar, their shifts from the mean plane being in the range 0.015–0.106 Å for $[La1(Pic)_3(TTD)]$ and 0.041–0.208 Å for $[La2(Pic)_3(TTD)]$. Lanthanum lies out of this plane by 0.232 Å (for La1) and 0.235 Å (for La2). In each of the $[La(Pic)_3(TTD)]$ monomers, TTD acts as a pentadentate ligand to form a ring-like coordination structure with its oxygen atoms together with one oxygen atom from the bidentate picrate (O26 for La1, O52 for La2) at the open side of the TTD chain (Figure 3).

The torsion angles in the TTD chain are listed in Table III. *Trans and gauche* conformations were reported to be most stable ones for C—O bonds and C—C bonds, respectively, in complexes of polyoxyethylene compounds of open-chain crown ethers.[12] In the present complex, the torsion angles around the C—O bonds are all close to ±180°, indicating that those bonds are nearly *trans*. The four O—C—C—O torsion angles are close to ±60°, suggesting that those bonds are approximately *gauche*, while the four O═C—C—O torsion angles (close to 0°) indicate those bonds are nearly in an *overlap* conformation not observed in other types of open-chain crown ether. The presence of the *overlap* conformation may be attributed to repulsion between the biphenylamine groups and the picrates.

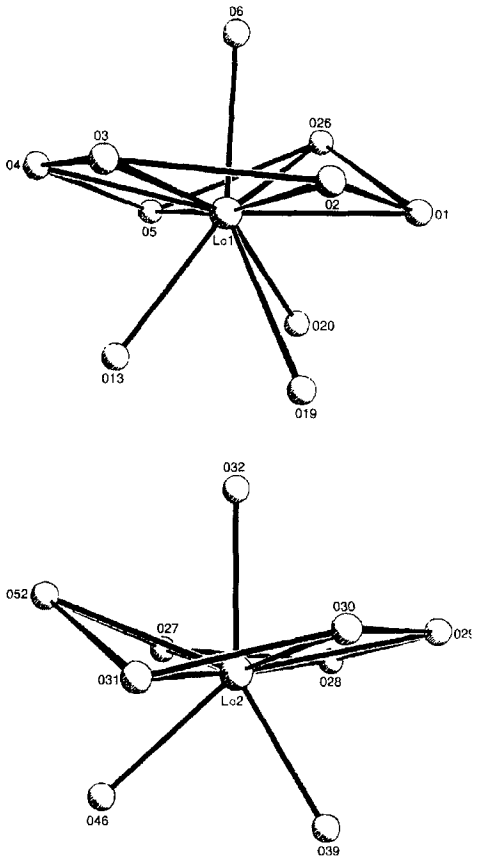


FIGURE 3 The ring-like coordination structures of the two independent monomers, designated La1 and La2, in [La)Pic)$_3$(TTD)].

TABLE III Selected torsion angles (deg) in the La1 and La2 monomers

[La1(Pic)$_3$(TTD)]		*[La2(Pic)$_3$(TTD)]*	
O1—C13—C14—O2	−2.3(19)	O27—C63—C64—O28	11.7(20)
O2—C15—C16—O3	58.6(15)	O28—C65—C66—O29	−48.2(19)
O3—C17—C18—O4	−60.8(16)	O29—C67—C68—O30	54.3(19)
O4—C19—C20—O5	−2.3(19)	O30—C69—C70—O31	−4.6(20)
C13—C14—O2—C15	178.4(12)	C63—C64—O28—C65	−165.5(13)
C14—O2—C15—C16	167.4(12)	C64—O28—C65—C66	−159.9(13)
C15—C16—O3—C17	170.1(13)	C65—C66—O29—C67	−172.1(16)
C16—O3—C17—C18	−177.8(13)	C66—O29—C67—C68	169.7(15)
C17—C18—O4—C19	−152.5(13)	C67—C68—O30—C69	154.3(15)
C18—O4—C19—C20	−159.8(12)	C68—O30—C69—C70	175.5(13)

The structural results above show that TTD acts as a multidentate ligand forming a ring-like coordination structure. Because of its superior flexibility, TTD exhibits a stable conformation that provides a cavity. The internal cavity formed by the coordinating oxygen atoms is suited for the uptake of a cation, while the nonpolar groups (CH_2 groups, aliphatic rings) form a lipophilic shell around the coordination sphere. The TTD molecule therefore shows high selectivity in complexation and lipophilicity, both of which make it a useful extractant and component sensor for Ba^{2+}. Furthermore, it can be shown experimentally that the structures and properties of the open-chain crown ethers complexes are closely related to many factors, such as the counter anion, the number of $\{CH_2—O—CH_2\}$ units and terminal group effects.[13–14] A further study concerned with these will be reported in following communications.

Acknowledgments

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