Synthesis, Characterization and Crystal Structure of Complexes of Thorium(IV) Nitrate with *N,N,N′,N′*-Tetraphenyl-3,6-dioxaoctanediamide[†]

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The solid powder and crystal complexes of thorium(IV) nitrate with *N,N,N′,N′*-tetraphenyl-3,6-dioxaoctanediamide (L), having the formulae $[Th(NO_3)_4(L)]$ and $[Th(NO_3)_4(L)]\cdot 2MeCN$, respectively, have been prepared and characterized by elemental analysis, molar conductance, IR and ^1H NMR spectra. The latter complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 14.156(3)$, $b = 14.595(2)$, $c = 20.713(3)$ Å, $\beta = 97.27(1)°$ and $Z = 4$. The final $R = 0.0376$ for 1857 independent observed $[I \geqslant 3\sigma(I)]$ reflections. The thorium atom is twelve-co-ordinated by oxygen atoms, eight from four bidentate nitrate groups and four from L, forming a distorted icosahedron. The compound L acts as a tetradentate ligand forming a half-ring co-ordination structure. The Th–O bonds average 2.515(5) (carbonyl oxygen), 2.565(5) (nitrate oxygen) and 2.653(5) Å (ether oxygen).

Non-cyclic polyethers, so-called open-chain crown ethers, show a high complexation selectivity towards s- and f-block metal ions, similar to those of crown ethers.[1] Open-chain crown ethers were used in the extraction and analysis of some metal ions.[2–4] Ding *et al.*[3] have reported the extraction of lighter lanthanide ions with five derivatives of ethylene glycol-*O,O′*-diacetamide, among which *N,N,N′,N′*-tetraphenyl-3,6-dioxaoctanediamide (L) has the largest separation factor, and both the factor and distribution ratio of lighter lanthanide ions for L are larger than those for dicyclohexyl-18-crown-6 ether (2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane).[5] Recently, compound L has been used in extraction of some actinide ions such as Am^{III} and Cm^{III}, the separation factors being as large as 5.6,[6] much larger than that for other common extracts.[7]

There are very few reports on the solid complexes of open-chain crown ethers with actinide ions and no crystal structure of those complexes. We present here the synthesis, characterization and crystal structure of the thorium(IV) nitrate complexes with L.

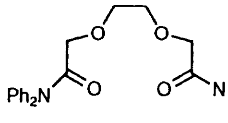
Experimental

Syntheses.—The compound L was prepared from triethylene glycol by a reported procedure [equation (1)].[8] The crude

$$HOC_2H_4OC_2H_4OC_2H_4OH \xrightarrow[\text{water, 70 °C}]{HNO_3,\ EtOH} HO_2CCH_2OC_2H_4OCH_2CO_2H \xrightarrow[C_6H_6]{SOCl_2} ClOCCH_2OC_2H_4OCH_2COCl \xrightarrow[C_6H_6]{NPh_2H,\ C_5H_5N} L \quad (1)$$

product was recrystallized from acetone–diethyl ether (1:1, v/v), m.p. 102 °C (lit.,[9] 95–97 °C); yield 76% (based on $HOC_2H_4OC_2H_4OC_2H_4OH$).

$[Th(NO_3)_4L]$. The compound L (0.18 g, 1.0 mmol) in $CHCl_3$ (15 cm^3) was added to a stirring solution of $Th(NO_3)_4\cdot 4H_2O$ (0.55 g, 1.0 mmol) in MeOH (20 cm^3). The reaction mixture was stirred at room temperature for 24 h, then concentrated to 20–30 cm^3. The precipitated solid was filtered off, washed with anhydrous ethanol and ether and dried over P_4O_{10} for 48 h. Yield: 0.83 g (88%) (Found: C, 37.15; H, 2.80; N, 8.60; Th, 24.30. $C_{30}H_{28}N_6O_{16}Th$ requires C, 37.50; H, 2.90; N, 8.75; Th, 24.15%). Molar conductance (MeCN, 10^{-3} mol dm^{-3}): 4.90 S cm^2 mol^{-1}.



L

The solid complex (0.29 g, 0.30 mmol) was dissolved in MeCN (10 cm^3) and the volume of the solution reduced by slow evaporation. After several weeks, crystals suitable for X-ray diffraction study deposited along the walls of the flask (Found: C, 38.70; H, 3.00; N, 10.30; Th, 22.20. $C_{30}H_{28}N_6O_{16}Th\cdot 2CH_3CN$ requires C, 39.20; H, 3.30; N, 10.75; Th, 22.25%). Molar conductance (MeCN, 10^{-3} mol dm^{-3}): 4.10 S cm^2 mol^{-1}.

Analysis and Physical Measurements.—The thorium ion was determined by ethylenediaminetetraacetate (edta) titration using xylenol orange as indicator; carbon, nitrogen and hydrogen were determined using a Carlo Erba 1106 elemental analyser. Infrared spectra were recorded on a Nicolet 170SX FT-IR instrument using KBr discs in the 250–4000 cm^{-1} region, ^1H NMR spectra on a FT-80A spectrometer in $(CD_3)_2SO$ solutions with $SiMe_4$ as internal standard.

X-Ray Crystallography for $[Th(NO_3)_4L]\cdot 2MeCN$.—*Crystal data.* $C_{34}H_{34}N_8O_{16}Th$, $M = 1042.7$, monoclinic, space group $P2_1/c$, $a = 14.156(3)$, $b = 14.595(2)$, $c = 20.713(3)$ Å, $\beta = 97.27(1)°$, $U = 4244.45(1)$ Å^3, $Z = 4$, $D_c = 1.63$ g cm^{-3}, λ(Mo-Kα) = 0.7107 Å, $F(000) = 2048$, μ(Mo-Kα) = 37.07 cm^{-1}.

Intensity data for a crystal 0.20 × 0.24 × 0.42 mm were measured on an R3M/E four-circle diffractometer with graphite-monochromatized Mo-Kα radiation using ω–2θ scans. 25 Reflections in the range $7 \leqslant 2\theta \leqslant 24°$ were used for measuring

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

lattice parameters. A total of 6139 unique reflections were collected in the range $2 \leqslant 2\theta \leqslant 45°$, of which 1857 satisfied the criterion $I \geqslant 3\sigma(I)$. Lorentz and polarization corrections were applied, but not for absorption.

The structure was solved by the Patterson method and subsequent Fourier difference techniques and refined by block-matrix least-squares procedures based on F. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen-atom positions were calculated. The hydrogen atoms were not refined but included in the calculation of structure factors. The weighting scheme was $w = [\sigma^2(F) + 0.000\,07F^2]^{-1}\{1 - \exp[-5(\sin\theta/\lambda)^2]\}$; final $R' = 0.0313$, $R = 0.0376$, $S = 0.898$. The final difference electron-density synthesis showed residual electron density from -1.07 to $+0.68$ e Å^{-3}. The final atom coordinates are given in Table 1. All calculations were performed with the SHELXTL program system.[10] Scattering factors for neutral atoms were taken from ref. 11.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The analytical data for the complexes conform to 1 : 1 metal-to-ligand stoichiometry, $Th(NO_3)_4L$ for the solid powders and $Th(NO_3)_4L{\cdot}2CH_3CN$ for the crystals. Both the powder and crystal complexes are soluble in Me_2SO, dimethylformamide, acetone and acetonitrile, slightly soluble in methanol, ethanol and chloroform, and sparingly soluble in benzene, ether and cyclohexane. The molar conductances of the complexes in acetonitrile indicate the presence of non-electrolytes.[12]

Infrared Spectra.—The IR spectra of the powder and crystal complexes indicate the same modes of the ligand and nitrate groups. The spectrum of free L shows bands at 1685 and 1132 cm^{-1} which may be assigned to ν(C=O) and ν(C–O–C), respectively. The two complexes exhibit shifts of 62 and 54 cm^{-1} for these two bands toward lower wavenumbers indicating that all the ether and carbonyl oxygens take part in co-ordination to the metal ions. The larger shift for ν(C=O) in the spectra of the complexes suggests that the Th–O(carbonyl) bond is stronger than that of the Th–O(ether).

The IR absorption bands corresponding to $\nu_4(B_1)$ and $\nu_5(B_2)$ of co-ordinated nitrate (C_{2v})[13] were observed at 1493 and 808 cm^{-1}, respectively, for the complexes. There was no band of free nitrate at about 1380 cm^{-1} in the spectra of the complexes.[14] The ν(C≡N) mode of MeCN appears at 2252 cm^{-1} for the crystal complex.

^{1}H NMR Spectra.—The spectrum of L exhibits an unresolved multiplet at δ 7.37, and two singlets at δ 4.01 and 3.57 assigned to protons of the Ph, $(O{=})CCH_2$ and C_2H_4 group, respectively. Upon co-ordination, all the signals move to lower field, those of $(O{=})CCH_2$ and C_2H_4 by 0.82 and 0.44 ppm, respectively, while the phenyl protons shift only by 0.18 ppm. This is due to the inductive effect of the Th–O(L) bonds. The larger shift for $(O{=})CCH_2$ than for C_2H_4 indicates that the Th–O(C=O) bond is stronger than that of Th–O(C–O–C). The proton signal of MeCN in the crystal complex is observed at δ 2.10.

Crystal Structure.—The crystal structure is composed of $[Th(NO_3)_4L]$ and two MeCN molecules linked by weak van der Waals forces. The structure of $[Th(NO_3)_4L]{\cdot}2MeCN$ is depicted in Fig. 1. The unit-cell contents are shown in Fig. 2, and selected bond lengths and angles are listed in Table 2.

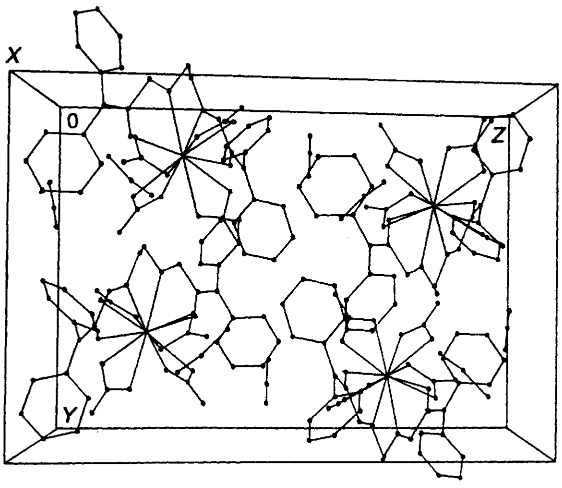

Fig. 2 Unit-cell contents for $[Th(NO_3)_4L]{\cdot}2MeCN$

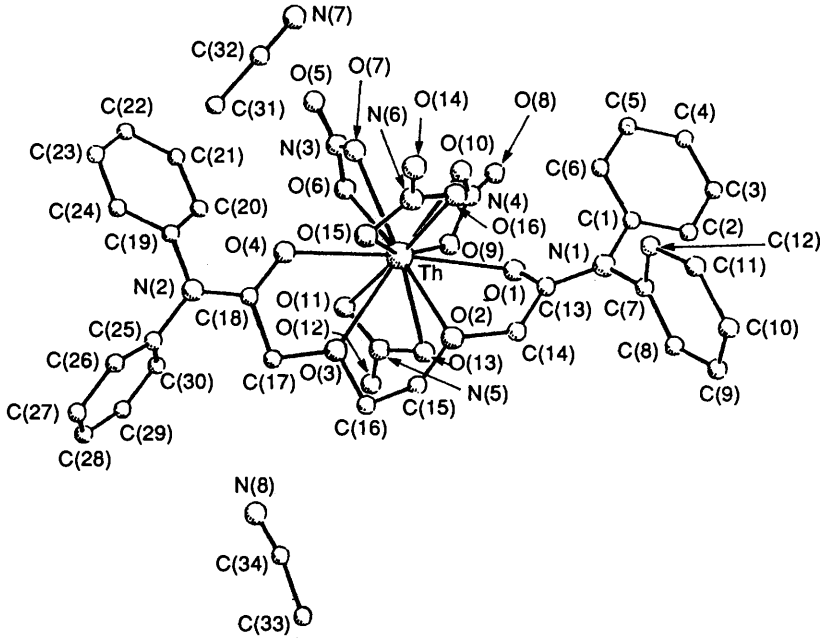

Fig. 1 Molecular structure of $[Th(NO_3)_4L]{\cdot}2MeCN$

Table 1 Final fractional atomic coordinates ($\times 10^4$) for $[\mathrm{Th(NO_3)_4L}]\cdot 2\mathrm{MeCN}$

Atom	*X/a*	*Y/b*	*Z/c*
Th	3574(1)	6861(1)	2092(1)
N(1)	6115(4)	7007(4)	951(3)
N(2)	1541(4)	5689(4)	3458(3)
N(3)	2961(4)	8385(4)	2914(3)
N(4)	3284(5)	8579(4)	1296(3)
N(5)	1903(4)	6037(4)	1240(3)
N(6)	5415(4)	6825(5)	3000(3)
N(7)	4865(7)	8859(7)	4585(4)
N(8)	1692(11)	2779(12)	2071(8)
O(1)	4601(3)	7033(3)	1195(2)
O(2)	4644(3)	5504(3)	1754(2)
O(3)	3216(3)	5119(3)	2362(6)
O(4)	2733(3)	6419(3)	3046(2)
O(5)	2738(5)	9028(4)	3231(3)
O(6)	2423(3)	8053(4)	2440(2)
O(7)	3773(3)	7995(3)	3044(2)
O(8)	3136(5)	9268(4)	982(3)
O(9)	2808(4)	7851(3)	1158(2)
O(10)	3906(4)	8529(3)	1793(2)
O(11)	1819(3)	6470(3)	1767(2)
O(12)	1220(4)	5715(5)	905(3)
O(13)	2744(3)	5967(3)	1092(2)
O(14)	6108(4)	6903(7)	3394(3)
O(15)	4727(3)	6295(4)	3074(2)
O(16)	5307(3)	7297(3)	2474(2)
C(1)	6099(5)	7935(4)	728(3)
C(2)	6327(6)	8138(6)	113(3)
C(3)	6335(7)	9032(5)	−92(4)
C(4)	6128(6)	9718(6)	305(4)
C(5)	5883(6)	9540(5)	917(4)
C(6)	5872(5)	8637(5)	1127(3)
C(7)	7002(5)	6494(5)	934(4)
C(8)	7084(6)	5850(6)	464(4)
C(9)	7933(7)	5397(7)	449(6)
C(10)	8685(7)	5601(8)	898(7)
C(11)	8605(7)	6226(8)	1372(7)
C(12)	7753(3)	6684(6)	1406(5)
C(13)	5375(5)	6624(4)	1184(3)
C(14)	5485(5)	5679(5)	1459(4)
C(15)	4617(6)	4575(5)	2004(4)
C(16)	3592(6)	4365(5)	2022(4)
C(17)	2397(5)	4887(5)	2683(4)
C(18)	2225(5)	5722(5)	3077(3)
C(19)	1279(5)	6500(5)	3799(3)
C(20)	952(6)	7269(6)	3463(4)
C(21)	679(7)	8023(7)	3804(5)
C(22)	742(7)	7997(8)	4463(5)
C(23)	1081(8)	7237(8)	4804(5)
C(24)	1345(6)	6473(7)	4476(4)
C(25)	936(5)	4893(6)	3474(4)
C(26)	1187(7)	4199(6)	3900(4)
C(27)	543(9)	3456(7)	3893(6)
C(28)	−283(8)	3457(8)	3459(6)
C(29)	−491(9)	4147(9)	3042(7)
C(30)	110(7)	4856(7)	3044(5)
C(31)	3565(10)	7663(10)	4617(6)
C(32)	4292(7)	8341(7)	4590(4)
C(33)	1562(12)	1603(18)	1132(11)
C(34)	1637(10)	2318(18)	1630(10)

Table 2 Selected bond distances (Å) and angles (°) for $[\mathrm{Th(NO_3)_4L}]\cdot 2\mathrm{MeCN}$

Th–O(1)	2.512(5)	Th–O(2)	2.641(5)	N(3)–O(7)	1.280(8)	N(4)–O(8)	1.200(9)
Th–O(3)	2.666(5)	Th–O(4)	2.517(5)	N(4)–O(9)	1.272(8)	N(4)–O(10)	1.269(7)
Th–O(6)	2.549(5)	Th–O(7)	2.563(5)	N(5)–O(11)	1.279(8)	N(5)–O(12)	1.211(8)
Th–O(9)	2.544(5)	Th–O(10)	2.570(5)	N(5)–O(13)	1.271(8)	N(6)–O(14)	1.199(8)
Th–O(11)	2.555(5)	Th–O(13)	2.600(5)	N(6)–O(15)	1.268(8)	N(6)–O(16)	1.281(8)
Th–O(15)	2.578(5)	Th–O(16)	2.561(4)	O(1)–C(13)	1.250(8)	O(2)–C(14)	1.428(9)
N(1)–C(1)	1.432(8)	N(1)–C(7)	1.466(9)	O(2)–C(15)	1.453(9)	O(3)–C(16)	1.444(9)
N(1)–C(13)	1.331(9)	N(2)–C(18)	1.326(9)	O(3)–C(17)	1.447(9)	O(4)–C(18)	1.253(9)
N(2)–C(19)	1.450(10)	N(2)–C(25)	1.446(10)	C(13)–C(14)	1.493(10)	C(15)–C(16)	1.48(1)
N(3)–O(5)	1.210(9)	N(3)–O(6)	1.261(7)	C(17)–C(18)	1.50(1)		
O(1)–Th–O(2)	58.3(1)	O(2)–Th–O(3)	58.0(2)	O(8)–N(4)–O(9)	121.8(6)	O(8)–N(4)–O(10)	122.9(6)
O(4)–Th–O(6)	64.5(2)	O(4)–Th–O(7)	65.0(2)	O(9)–N(4)–O(10)	115.3(6)	O(11)–N(5)–O(12)	121.8(6)
O(6)–Th–O(7)	49.7(1)	O(1)–Th–O(9)	67.2(1)	O(11)–N(5)–O(13)	115.9(5)	O(12)–N(5)–O(13)	122.2(6)
O(6)–Th–O(9)	66.5(2)	O(1)–Th–O(10)	65.6(1)	O(14)–N(6)–O(15)	123.4(7)	O(14)–N(6)–O(16)	121.7(7)
O(6)–Th–O(10)	64.2(2)	O(7)–Th–O(10)	64.4(1)	O(15)–N(6)–O(16)	114.9(5)	Th–O(1)–C(13)	123.8(4)
O(9)–Th–O(10)	49.6(1)	O(3)–Th–O(11)	68.8(1)	Th–O(2)–C(14)	121.1(4)	Th–O(2)–C(15)	124.3(4)
O(4)–Th–O(11)	67.0(1)	O(6)–Th–O(11)	65.9(1)	C(14)–O(2)–C(15)	112.3(5)	Th–O(3)–C(16)	122.2(4)
O(9)–Th–O(11)	67.6(2)	O(1)–Th–O(13)	72.9(1)	Th–O(3)–C(17)	120.3(4)	C(16)–O(3)–C(17)	114.3(5)
O(2)–Th–O(13)	68.2(1)	O(3)–Th–O(13)	67.0(1)	Th–O(4)–C(18)	125.4(4)	Th–O(6)–N(3)	97.9(4)
O(9)–Th–O(13)	64.7(2)	O(11)–Th–O(13)	49.6(2)	Th–O(7)–N(3)	96.7(3)	Th–O(9)–N(4)	98.1(4)
O(2)–Th–O(15)	69.0(2)	O(3)–Th–O(15)	69.3(1)	Th–O(10)–N(4)	96.9(4)	Th–O(11)–N(5)	98.2(4)
O(4)–Th–O(15)	67.2(2)	O(7)–Th–O(15)	66.6(2)	Th–O(13)–N(5)	96.3(4)	Th–O(15)–N(6)	97.3(4)
O(1)–Th–O(16)	65.3(1)	O(2)–Th–O(16)	73.1(1)	Th–O(16)–N(6)	97.8(4)	N(1)–C(13)–O(1)	122.5(6)
O(7)–Th–O(16)	66.0(1)	O(10)–Th–O(16)	69.0(2)	N(1)–C(13)–C(14)	118.5(6)	O(1)–C(13)–C(14)	118.9(6)
O(15)–Th–O(16)	59.4(2)	C(1)–N(1)–C(7)	117.0(5)	O(2)–C(14)–C(13)	106.0(6)	O(2)–C(15)–C(16)	105.7(6)
C(1)–N(1)–C(13)	122.3(5)	C(7)–N(1)–C(13)	120.7(5)	O(3)–C(16)–C(15)	106.1(6)	O(3)–C(17)–C(18)	104.7(6)
C(18)–N(2)–C(19)	120.7(6)	C(18)–N(2)–C(25)	121.5(6)	N(2)–C(18)–O(4)	121.8(7)	N(2)–C(18)–C(17)	118.4(6)
C(19)–N(2)–C(25)	117.1(6)	O(5)–N(3)–O(6)	123.2(6)	O(4)–C(18)–C(17)	119.8(6)		
O(5)–N(3)–O(7)	121.3(6)	O(6)–N(3)–O(7)	115.0(5)				

The thorium is twelve-co-ordinated by 12 oxygen atoms, eight from four bidentate nitrate groups and four from L. The thorium co-ordination polyhedron is a distorted icosahedron (Fig. 3). The twelve Th–O bonds were divided into three classes based on their lengths. The average distance is 2.571(5) Å and the average values of the three classes are in the order Th–O(C=O) [2.515(5)] < Th–O(NO$_3$) [2.565(5)] < Th–O(C–O–C) [2.653(5) Å]. This confirms that the Th–O(C=O) bond is stronger than Th–O(C–O–C), inferred from the IR and ^{1}H NMR spectral analyses.

The compound L acts as a tetradentate ligand forming a half-ring co-ordination structure. Its four oxygen atoms are not quite coplanar, their deviations from the mean plane being in the range 0.176–0.367 Å, thorium lies out of this plane by 0.116 Å.

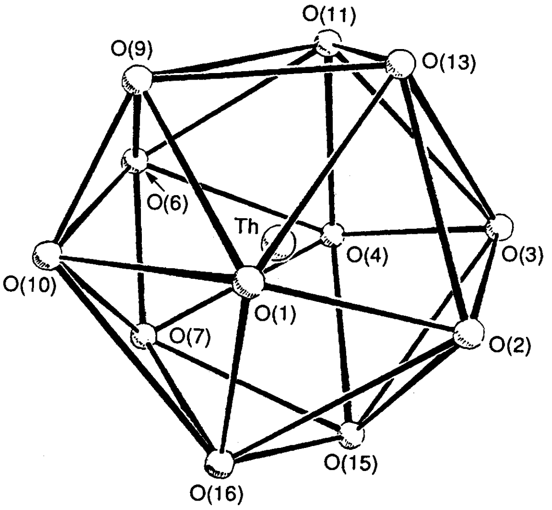

Fig. 3 The co-ordination polyhedron about the thorium atom in [Th(NO$_3$)$_4$L]·2MeCN

Two nitrates, N(5)O$_3$ and N(6)O$_3$, co-ordinate from below and above this plane, the other two from the open side of the L chain. Each of the nitrates is almost planar, but they show a little departure from the idealized C_{2v} local symmetry expected for bidentate nitrates.

Torsion angles in the L chain are listed in Table 3. The *trans* and *gauche* conformations were reported to be the most stable ones for C–O and C–C bonds, respectively, in complexes of polyoxyethylene compounds[15] of open-chain crown ethers. 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 angle around the C(15)–C(16) bond is close to −60° suggesting that this bond is approximately *gauche*, while the angles (close to 0°) around C(13)–C(14) and (17)–C(18) indicate that those bonds are nearly in the overlap conformation which was not observed in other types of open-chain crown ethers.

Table 3 Selected torsion angles (°) for [Th(NO$_3$)$_4$L]·2MeCN

O(1)–C(13)–C(14)–O(2)	−6.7(8)
O(2)–C(15)–C(16)–O(3)	−50.8(8)
O(3)–C(17)–C(18)–O(4)	2.7(8)
C(13)–C(14)–O(2)–C(15)	−175.8(5)
C(14)–O(2)–C(15)–C(16)	−155.9(6)
C(15)–C(16)–O(3)–C(17)	153.8(6)
C(16)–O(3)–C(17)–C(18)	171.9(5)

The presence of this conformation may be attributed to the repulsion between the diphenylamine groups and the nitrates.

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