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A structural study of (dibenzyldiaza-18-crown-6) lanthanum(III) thiocyanate

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Abstract

The structure of the complex $La(NCS)_3C_{26}H_{38}N_2O_4$ (**1**) was determined by single-crystal X-ray diffraction and the structure of the coordinating ligand, $C_{26}H_{38}N_2O_4$ (**2**), was studied by the semi-empirical PM3 method. The bonding around La consists of a primary coordination of three thiocyanate N atoms and a secondary coordination of two N atoms and four O atoms of the macrocycle. The primary coordination about La gives an almost planar trigonal configuration that bisects the plane of the macrocycle with La lying in the centre of the macrocycle cavity. The benzyl groups that are attached to the macrocycle are in *syn* conformation with respect to the macrocycle plane with one of the La–NCS bonds pointing above the plane and the other two La–NCS bonds pointing below the plane in the direction of the benzyl groups. The PM3 calculation shows that the optimised diazacrown has an open structure of a pseudo D_{2d} symmetry with the two benzyl side-arms positioned away from the cavity. © 1997 Elsevier Science B.V.

Keywords: Dibenzyldiaza-18-crown-6; Lanthanum thiocyanate; PM3 calculation; X-ray crystallography

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1. Introduction

The coordination chemistry of metals with crown ethers and azacrown ethers has received considerable attention because of the ability of the macrocycles to act as excellent complexing agents. Studies on these interactions have led to greater understanding of the various factors such as cavity size, substituent effects, shape, flexibility, and donor atoms, that influence the selectivities of macrocycles for the cations[1–3]. There have been numerous reports on the X-ray crystal structure determination of metal ion crown-ether complexes covering virtually all classes of metal ions[4–6] including a number of lanthanum crown-ether structures. The structure adopted by the metal ion crown-ether complex is dependent on the cavity size—metal ion fit ranges from the model cation fitting directly into the cavity and interacting with all the donor atoms equally to that of out-of-cavity coordination when the metal ion is too large to fit into the cavity[7]. Crown ethers bearing side-arms, or lariat ethers, have also been much studied especially with respect to their properties as flexible and dynamic cation binders which utilize their side-arms and macro-rings cooperatively[8].

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Since relatively few studies have been reported on the structure of complexes of diazacrown with the lanthanides[9,10], we have prepared a complex of lanthanum thiocyanate with dibenzyldiaza-18-crown-6 and studied its structure by X-ray crystallography. In addition, we have performed a semi-empirical quantum chemical PM3 calculation on the parent diazacrown since it does not exist as suitable crystals for X-ray crystal structure determination; such an effort would enable us to compare the structural features of the diazacrown before and after coordination with the lanthanum salt.

2. Experimental

2.1. Preparation of the complex of La(NCS)$_3$ with dibenzyldiaza-18-crown-6

Equimolar amounts of lanthanum thiocyanate and dibenzyldiaza-18-crown-6 were dissolved in a 1:1 mixture of warm methanol and acetonitrile. The resulting solution was filtered immediately and on cooling yielded colourless crystals of the complex.

2.2. X-ray crystallographic studies

The X-ray data collection was carried out by an automated Enraf–Nonius CAD-4 diffractometer with graphite-monochromated MoK$_\alpha$ (λ = 0.7170 Å) radiation, and the determination of the crystal class, orientation matrix and cell parameters were performed according to standard procedures [11]. The intensities were recorded at approximately 27°C up to a $2\Theta_{max}$ of 50°. The unit cell constants for the structure lattice were obtained from the angular settings of 25 strong reflections. Crystal decay was monitored by using three standard random reflections. Absorption correction was neglected. The crystal data and experimental details are summarized in Table 1. The crystal structure was solved by the heavy atom method from a Patterson synthesis and all the remaining non-hydrogen atoms were located from subsequent difference–Fourier maps. The H atoms were fixed geometrically and allowed to ride on their respective parent atoms and were included in structure–factor calculations. The structure solution and refinement were performed using the SHELXS86 and SHELXL93 programs [12] on a 486 personal computer.

Table 1
Crystal data for $La(NCS)_3C_{26}H_{38}N_2O_4$

Formula weight	755.73
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 15.5855(8) Å α = 90° b = 9.6801(5) Å β = 94.188(4)° c = 21.8962(10) Å γ = 90°
Volume	3294.6(3) Å^3
Z	4
Density (calculated)	1.524 mg m^{-3}
Absorption coefficient	1.527 mm^{-1}
$F(000)$	1536
Crystal size	0.14 × 0.43 × 0.50 mm^3
Θ range for data collection	1.31 to 24.98°
Index ranges	$-18 \le h \le 0, -11 \le k \le 0, -25 \le l \le 26$
Reflections collected	6027
Independent reflections	5798 [R(int) = 0.0260]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5798/0/379
Goodness-of-fit on F^2	0.816
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0403, $wR2$ = 0.1057
R indices (all data)	$R1$ = 0.0487, $wR2$ = 0.1125
Largest diff. peak and hole	1.424 and − 1.710 e Å^{-3}

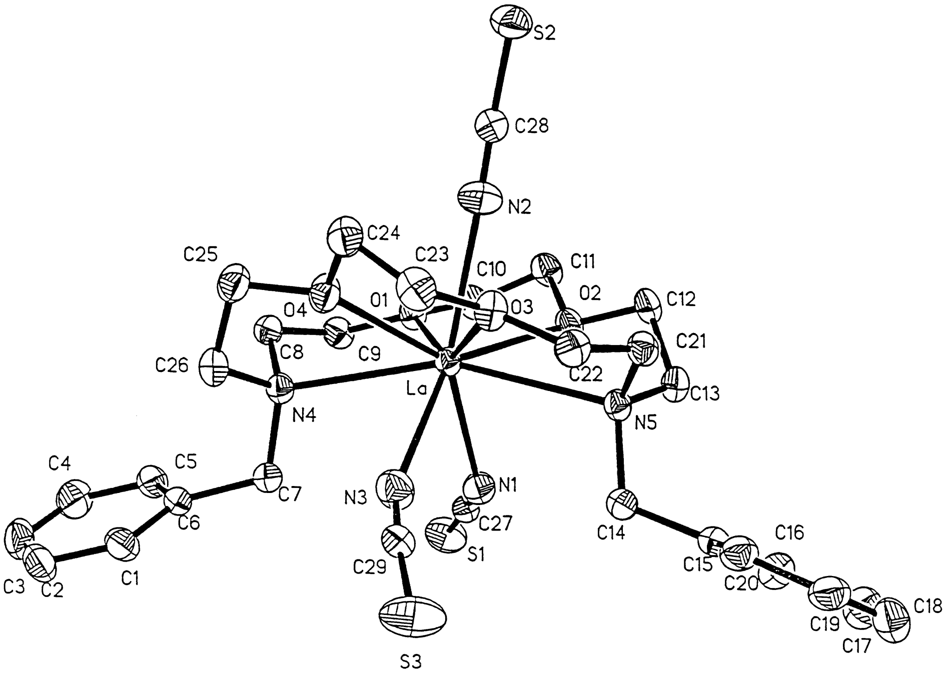

Fig. 1. The molecular structure of La(NCS)$_3$.C$_{26}$H$_{28}$N$_2$O$_4$ showing La coordination.

2.3. Semi-empirical quantum chemical optimization

The azacrown structure was optimized in its lowest energy state using the semiempirical quantum chemical PM3 method [13] available in the MOPAC 6.0 package [14]. The initial structure of the azacrown was built using the Insight II Builder module [15] resident in a Silicon Graphics Indigo workstation and partially minimized using the molecular mechanics CVFF force-field method[15]. The partially optimized structure was then converted into a MOPAC Z-matrix input file and was fully optimized without any constraints. Safety checks during the optimization were also disabled. The key words

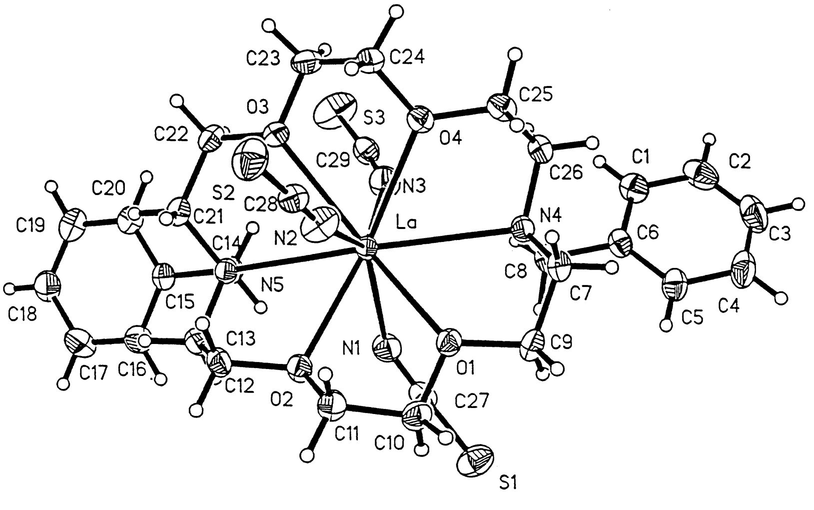

Fig. 2. The molecular structure of La(NCS)$_3$.C$_{26}$H$_{28}$N$_2$O$_4$.

PRECISE and GEO-OK were used in the MOPAC calculation. PRECISE increases the criteria for terminating optimizations. GEO-OK overrides the termination of jobs which results when two atoms are found to be within 0.8 Å of each other. The full optimization was performed on a Cray J90 at the CADCAM Centre, University of Malaya.

3. Results and discussion

The molecular structure of **1** is shown in Figs. 1 and 2. The atomic coordinates and selected bond distances, angles and torsion angles are given in Tables 1 to 5. The packing of the molecule is shown in Fig. 3. The molecular structure of **2** is shown in Fig. 4(a) and (b).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). *U*(eq) is defined as one third of the trace of the orthogonalized *U*ij tensor

	x	*y*	*z*	*U*(eq)
La	2290(1)	2117(1)	1609(1)	32(1)
S(1)	5469(1)	2088(2)	1483(1)	70(1)
S(2)	–275(1)	–1352(2)	1015(1)	66(1)
S(3)	1860(1)	–2838(2)	2220(1)	92(1)
O(1)	3219(2)	–88(3)	1685(1)	40(1)
O(2)	2703(2)	978(3)	587(1)	42(1)
O(3)	716(2)	3143(3)	1463(1)	44(1)
O(4)	1296(2)	1896(4)	2494(1)	51(1)
N(1)	3775(3)	2967(4)	1370(2)	50(1)
N(2)	1188(3)	221(4)	1286(2)	61(1)
N(3)	2358(3)	–5572(5)	2140(2)	60(1)
N(4)	3084(2)	1522(4)	2761(2)	38(1)
N(5)	1886(2)	3645(4)	533(2)	36(1)
C(1)	4109(3)	3295(6)	3972(2)	54(1)
C(2)	4481(4)	3171(7)	4569(3)	68(2)
C(3)	5016(4)	2110(8)	4728(3)	75(2)
C(4)	5217(3)	1151(7)	4305(3)	69(2)
C(5)	4861(3)	1265(6)	3704(2)	54(1)
C(6)	4290(3)	2312(5)	3535(2)	43(1)
C(7)	3874(3)	2394(5)	2890(2)	43(1)
C(8)	3297(3)	33(5)	2767(2)	43(1)
C(9)	3757(3)	–429(5)	2227(2)	45(1)
C(10)	3541(3)	689(5)	1149(2)	50(1)
C(11)	2879(3)	–467(5)	624(2)	49(1)
C(12)	2163(3)	1363(5)	58(2)	46(1)
C(13)	2219(3)	2916(4)	4(2)	44(1)
C(14)	2282(3)	5063(5)	598(2)	42(1)
C(15)	2080(3)	6051(4)	72(2)	39(1)
C(16)	2593(3)	–1120(5)	4576(2)	53(1)
C(17)	2399(4)	–2054(6)	4102(3)	63(1)
C(18)	1712(4)	–2933(5)	4122(3	61(1)
C(19)	1216(3)	7891(5)	–385(3)	54(1)
C(20)	1403(3)	6959(4)	83(2)	46(1)
C(21)	937(3)	3741(5)	448(2)	42(1)
C(22)	525(3)	4172(5)	1012(2)	44(1)
C(23)	233(3)	3289(6)	1993(2)	53(1)
C(24)	384(3)	2030(6)	2379(2)	51(1)
C(25)	1588(3)	1248(6)	3060(2)	52(1)
C(26)	2466(3)	1792(5)	3229(2)	48(1)
C(27)	4481(3)	2609(5)	1410(2)	43(1)
C(28)	584(3)	–444(5)	1181(2)	43(1)
C(29)	2166(3)	–4438(5)	2199(2)	45(1)

Table 3
Bond lengths (Å), angles (°) and torsion angles (°) with e.s.d. in parentheses

Atoms	X-ray	PM3	Atoms	X-ray	PM3	Atoms	X-ray	PM3
La–O(1)	2.578(3)	–	N(1)–La–N(5)	79.0(1)	–	C(7)–N(4)–La	111.0(2)	–
La–O(2)	2.616(3)	–	N(1)–C(27)–S(1)	178.6(4)	–	C(7)–N(4)–La	107.1(2)	–
La–O(3)	2.645(3)	–	N(2)–LA–O(1)	77.8(1)	–	C(8)–N(4)–C(7)	111.4(3)	115.01
La–O(4)	2.577(3)	–	N(2)–La–O(2)	70.5(1)	–	C(8)–N(4)–C(26)	108.9(3)	113.83
La–N(1)	2.548(4)	–	N(2)–La–O(3)	68.9(1)	–	C(9)–O(1)–La	122.3(2)	–
La–N(2)	2.577(4)	–	N(2)–La–N(4)	110.1(1)	–	C(10)–O(1)–C(9)	111.3(3)	116.21
La–N(3)	2.519(4)	–	N(2)–La–N(5)	92.3(1)	–	C(10)–O(1)–La	120.8(2)	–
La–N(4)	2.787(3)	–	N(2)–C(28)–S(2)	178.3(5)	–	C(11)–O(2)–C(12)	113.6(3)	115.03
La–N(5)	2.814(3)	–	N(3)–C(29)–S(3)	174.9(4)	–	C(11)–O(2)–La	115.0(2)	–
S(1)–C(27)	1.617(5)	–	N(3)–La–N(1)	78.4(1)	–	C(12)–O(2)–La	114.5(2)	–
S(2)–C(28)	1.620(5)	–	N(3)–La–N(2)	139.8(1)	–	C(13)–N(5)–C(14)	110.0(3)	111.6
S(3)–C(29)	1.621(5)	–	N(3)–La–O(1)	134.4(1)	–	C(13)–N(5)–La	109.5(2)	–
O(1)–C(9)	1.440(5)	1.48	N(3)–La–O(2)	139.8(1)	–	C(14)–N(5)–La	109.5(2)	–
O(1)–C(10)	1.433(5)	1.45	N(3)–La–O(3)	74.3(1)	–	C(15)–C(20)–C(19)	121.8(5)	122.77
O(2)–C(11)	1.427(5)	1.46	N(3)–La–O(4)	74.5(1)	–	C(16)–C(15)–C(14)	121.6(4)	123.14
O(2)–C(12)	1.431(5)	1.48	N(3)–La–N(4)	76.4(1)	–	C(17)–C(16)–C(15)	120.4(5)	122.65
O(3)–C(22)	1.420(5)	1.49	N(3)–La–N(5)	85.4(1)	–	C(17)–C(18)–C(19)	119.4(5)	120.01
O(3)–C(23)	1.436(5)	1.47	N(4)–La–N(S)	157.5(1)	–	C(18)–C(17)–C(16)	120.5(5)	119.58
O(4)–C(24)	1.433(5)	1.46	N(4)–C(7)–C(6)	115.8(3)	129.86	C(18)–C(19)–C(20)	120.2(5)	119.44
O(4)–C(25)	1.432(5)	1.48	N(4)–C(8)–C(9)	113.8(3)	118.75	C(20)–C(15)–C(14)	120.6(4)	122.83
N(1)–C(27)	1.151(6)	–	N(4)–C(26)–C(25)	113.5(4)	117.55	C(20)–C(15)–C(16)	117.7(4)	115.63
N(2)–C(28)	1.150(6)	–	N(5)–C(13)–C(12)	112.9(3)	117.55	C(21)–N(5)–La	107.4(2)	–
N(3)–C(29)	1.148(6)	–	N(5)–C(14)–C(15)	116.4(3)	131.08	C(21)–N(5)–C(13)	109.6(3)	111.6
N(4)–C(7)	1.503(5)	1.56	N(5)–C(21)–C(22)	113.5(3)	119.18	C(21)–N(5)–C(14)	110.7(3)	113.64
N(4)–C(8)	1.480(5)	1.51	O(1)–La–O(2)	62.3(8)	–	C(22)–O(3)–C(23)	113.6(3)	112.76
N(4)–C(26)	1.479(5)	1.53	O(1)–La–O(3)	146.2(9)	–	C(22)–O(3)–La	119.5(2)	–
N(5)–C(13)	1.480(5)	1.53	O(1)–La–N(4)	63.9(9)	–	C(23)–O(3)–La	118.4(3)	–
N(5)–C(14)	1.507(5)	1.57	O(1)–La–N(5)	125.5(9)	–	C(24)–O(4)–C(25)	116.1(3)	120.09
N(5)–C(21)	1.480(5)	1.51	O(1)–C(9)–C(8)	107.3(3)	114.09	C(24)–O(4)–La	120.3(3)	–
C(1)–C(2)	1.396(7)	1.41	O(1)–C(10)–C(11)	107.9(3)	115.71	C(25)–O(4)–La	121.1(2)	–
C(1)–C(6)	1.391(6)	1.43	O(2)–C(11)–C(10)	107.6(3)	116.31	C(26)–N(4)–C(7)	109.6(3)	116.86
C(2)–C(3)	1.351(9)	1.41	O(2)–C(12)–C(13)	106.7(3)	113.76	C(26)–N(4)–La	108.8(2)	–
C(3)–C(4)	1.364(9)	1.40	O(2)–La–N(5)	63.9(9)	–	C(27)–N(1)–La	139.8(4)	–
C(4)–C(5)	1.393(7)	1.41	O(3)–La–N(5)	63.4(9)	–	C(28)–N(2)–La	166.7(4)	–
C(5)–C(6)	1.379(7)	1.42	O(3)–C(22)–C(21)	107.4(3)	118.64	C(29)–N(3)–La	154.0(4)	–
C(6)–C(7)	1.515(6)	1.62	O(3)–C(23)–C(24)	108.0(4)	119.13	N(4)–C(8)–C(9)–O(1)	−57.6(4)	99.55
C(8)–C(9)	1.495(6)	1.56	O(2)–La–O(3)	109.8(9)	–	C(8)–C(9)–O(1)–C(11)	−170.6(0)	128.31
C(10)–C(11)	1.503(6)	1.56	O(2)–La–N(4)	124.5(9)	–	C(9)–O(1)–C(10)–C(11)	−171.6(3)	−178.84
C(12)–C(13)	1.511(6)	1.55	O(3)–La–N(4)	122.2(9)	–	O(1)–C(10)–C(11)–O(2)	54.9(3)	−76.04
C(14)–C(15)	1.512(6)	1.63	O(4)–La–N(2)	73.9(1)	–	C(10)–C(11)–O(2)–C(12)	172.5(5)	167.95
C(15)–C(16)	1.397(6)	1.42	O(4)–La–O(1)	104.4(1)	–	C(11)–O(2)–C(12)–C(13)	−163.3(5)	174.24
C(15)–C(20)	1.374(6)	1.43	O(4)–La–O(2)	143.13(1)	–	O(2)–C(12)–C(13)–N(5)	−63.0(3)	156.45
C(16)–C(17)	1.392(7)	1.41	O(4)–La–O(3)	61.2(9)	–	C(12)–C(13)–N(5)–C(21)	−82.0(0)	−91.64
C(17)–C(18)	1.373(8)	1.40	O(4)–La–N(4)	63.5(9)	–	C(13)–N(5)–C(21)–C(22)	167.1(5)	70.29
C(18)–C(19)	1.374(8)	1.41	O(4)–La–N(5)	124.3(9)	–	N(5)–C(21)–C(22)–O(3)	−62.2(2)	−97.71
C(19)–C(20)	1.381(7)	1.41	O(4)–C(24)–C(23)	106.6(4)	–	C(21)–C(22)–O(3)–C(23)	−169.2(6)	−175.47
C(21)–C(22)	1.492(6)	1.56	O(4)–C(25)–C(26)	106.8(4)	–	C(22)–O(3)–C(23)–C(24)	−170.8(5)	172.17
C(23)–C(24)	1.490(7)	1.56	C(1)–C(6)–C(7)	120.7(4)	121.42	O(3)–C(23)–C(24)–O(4)	54.6(0)	62.19
C(25)–C(26)	1.487(6)	1.57	C(2)–C(3)–C(4)	120.7(5)	120.00	C(23)–C(24)–O(4)–C(25)	150.4(1)	122.73
N(1)–La–O(1)	76.5(1)	–	C(2)–C(3)–C(1)	120.7(5)	119.48	C(24)–O(4)–C(25)–C(26)	−153.3(5)	136.98
N(1)–La–O(2)	71.1(1)	–	C(3)–C(4)–C(5)	119.4(6)	119.60	O(4)–C(25)–C(26)–N(4)	−58.8(3)	142.70
N(1)–La–O(3)	134.7(1)	–	C(5)–C(6)–C(1)	118.5(4)	115.63	C(25)–C(26)–N(4)–C(8)	−71.9(1)	−44.53
N(1)–La–O(4)	141.9(1)	–	C(5)–C(6)–C(7)	120.8(4)	122.83	C(26)–N(4)–C(8)–C(9)	167.0(9)	−59.18
N(1)–La–N(2)	140.5(1)	–	C(6)–C(1)–C(2)	119.6(5)	122.71			
N(1)–La–N(4)	84.4(1)	–	C(6)–C(5)–C(4)	121.0(5)	122.57			

Table 4
Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + \ldots + 2hka^*b^*U12]$

	*U*11	*U*22	*U*33	*U*23	*U*13	*U*12
La	33(1)	32(1)	30(1)	0(1)	0(1)	2(1)
S(1)	48(1)	72(1)	89(1)	−11(1)	−2(1)	1(1)
S(2)	50(1)	70(1)	74(1)	5(1)	−9(1)	−14(1)
S(3)	86(1)	43(1)	147(2)	−21(1)	8(1)	3(1)
O(1)	47(2)	35(2)	38(2)	0(1)	−2(1)	10(1)
O(2)	51(2)	37(2)	36(2)	−7(1)	4(1)	6(1)
O(3)	42(2)	49(2)	41(2)	3(1)	6(1)	13(1)
O(4)	38(2)	78(2)	37(2)	11(2)	4(1)	−2(2)
N(1)	46(2)	57(3)	47(2)	2(2)	4(2)	−7(2)
N(2)	52(2)	46(2)	84(3)	−8(2)	1(2)	−3(2)
N(3)	72(3)	50(3)	56(3)	−7(2)	−1(2)	5(2)
N(4)	40(2)	41(2)	31(2)	2(2)	0(1)	0(2)
N(5)	38(2)	36(2)	33(2)	1(2)	−2(1)	4(2)
C(1)	54(3)	58(3)	51(3)	−9(2)	1(2)	−9(2)
C(2)	65(3)	92(4)	49(3)	−24(3)	9(3)	−21(3)
C(3)	71(4)	111(6)	41(3)	9(3)	−9(3)	−22(4)
C(4)	55(3)	86(4)	62(3)	20(3)	−18(3)	−3(3)
C(5)	51(3)	59(3)	50(3)	4(2)	−11(2)	−6(2)
C(6)	44(2)	46(2)	37(2)	2(2)	−2(2)	−11(2)
C(7)	48(2)	44(2)	36(2)	3(2)	−2(2)	−7(2)
C(8)	50(2)	40(2)	38(2)	6(2)	−3(2)	−2(2)
C(9)	46(2)	40(2)	48(3)	3(2)	−10(2)	8(2)
C(10)	56(3)	44(2)	48(3)	−6(2)	−2(2)	14(2)
C(11)	61(3)	37(2)	47(3)	−9(2)	−5(2)	9(2)
C(12)	54(3)	50(3)	31(2)	−7(2)	−5(2)	6(2)
C(13)	51(3)	45(3)	34(2)	2(2)	4(2)	6(2)
C(14)	45(2)	39(2)	42(2)	−1(2)	−3(2)	−3(2)
C(15)	44(2)	35(2)	39(2)	−1(2)	−3(2)	−5(2)
C(16)	57(3)	49(3)	53(3)	4(2)	9(2)	−1(2)
C(17)	83(4)	58(3)	50(3)	−3(2)	15(3)	2(3)
C(18)	77(4)	52(3)	53(3)	−8(2)	−9(3)	16(3)
C(19)	53(3)	39(3)	69(3)	5(2)	−10(2)	−5(2)
C(20)	47(3)	39(2)	52(3)	0(2)	0(2)	0(2)
C(21)	40(2)	42(2)	42(2)	2(2)	−5(2)	3(2)
C(22)	36(2)	45(2)	51(3)	6(2)	−3(2)	7(2)
C(23)	40(2)	69(3)	52(3)	−11(3)	10(2)	9(2)
C(24)	34(2)	75(4)	44(3)	2(2)	8(2)	2(2)
C(25)	48(3)	68(3)	41(2)	8(2)	9(2)	−1(2)
C(26)	53(3)	56(3)	33(2)	3(2)	3(2)	5(2)
C(27)	48(3)	47(2)	34(2)	−3(2)	5(2)	−13(2)
C(28)	41(2)	44(2)	45(2)	−1(2)	4(2)	3(2)
C(29)	53(3)	44(3)	39(2)	−7(2)	1(2)	−6(2)

The lanthanum thiocyanate salt exists as an isolated (individual) entity in the centre of the hole of the macrocycle. The three thiocyanate N atoms surround the La cation in a near planar trigonal arrangement with the La ion being slightly out-of-plane (sum of 358.74° for the N–La–N angle around La) and with unequally distributed N–La–N bond angles. The trigonal plane is perpendicular to and bisects the plane of macrocycle indicating the presence of a C_2 symmetry. The bonding around La is made up of primary coordination of the three thiocyanate N atoms and secondary coordination of the two N atoms and four O atoms of the macrocycle to give La a distorted nanohedral environment. The

Table 5
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters (Å$^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
H(1)	3743(3)	4029(6)	3866(2)	65
H(2)	4358(4)	3825(7)	4861(3)	82
H(3)	5249(4)	2034(8)	5130(3)	90
H(4)	5588(3)	427(7)	4416(3)	83
H(5)	5011(3)	626(6)	3413(2)	65
H(7A)	3722(3)	3350(5)	2803(2)	51
H(7B)	4297(3)	2125(5)	2608(2)	51
H(8A)	2769(3)	–494(5)	2780(2)	51
H(8B)	3653(3)	–173(5)	3138(2)	51
H(9A)	4308(3)	38(5)	2222(2)	55
H(9B)	3859(3)	–1417(5)	2247(2)	55
H(10A)	3643(3)	–1669(5)	1212(2)	60
H(10B)	4080(3)	–255(5)	1062(2)	60
H(11A)	3096(3)	–791(5)	245(2)	58
H(11B)	2358(3)	–974(5)	692(2)	58
H(12A)	1574(3)	1081(5)	105(2)	55
H(12B)	2358(3)	924(5)	–305(2)	55
H(13A)	2814(3)	3177(4)	–29(2)	52
H(13B)	1893(3)	3208(4)	–368(2)	52
H(14A)	2901(3)	4957(5)	654(2)	51
H(14B)	2093(3)	5481(5)	968(2)	51
H(16)	3066(3)	–539(5)	4562(2)	63
H(17)	2739(4)	–2082(6)	3770(3)	76
H(18)	1582(4)	–3552(5)	3804(3)	73
H(19)	753(3)	8493(5)	–366(3)	65
H(20)	1061(3)	6944(4)	414(2)	56
H(21A)	708(3)	2849(5)	317(2)	50
H(21B)	783(3)	4400(5)	125(2)	50
H(22A)	750(3)	5059(5)	1154(2)	53
H(22B)	–92(3)	4255(5)	927(2)	53
H(23A)	–375(3)	3382(6)	1871(2)	64
H(23B)	419(3)	4106(6)	2223(2)	64
H(24A)	112(3)	228(6)	2761(2)	61
H(24B)	148(3)	1222(6)	2166(2)	90
H(25A)	1605(3)	253(6)	3011(2)	63
H(25B)	1205(3)	1468(6)	3376(2)	63
H(26A)	2430(3)	2781(5)	3293(2)	57
H(26B)	2683(3)	1376(5)	3612(2)	57

macro-ring donor atoms adopt a twist-boat conformation encapsulating the La ion. The primary bond distances for La–N range from 2.519 to 2.577 Å while the secondary La–N bond distances are considerably longer, ranging from 2.787 to 2.814 Å. The secondary La–O bond distances range from 2.577 to 2.645 Å and are much longer compared with primary bonds found in lanthanum oxyhalides (average 2.40 Å). These longer secondary bond distances reflect the weaker electronic interactions between the La(NCS) moiety and the macrocycle arising from steric requirements. Similar observations have been made for primary and secondary bond distances for similar complexes such as lanthanum nitrate with the tetraoxadiaza macrocycle[9]. The size of the hole of the macrocycle as measured across the opposite-facing O1 and O3 atoms is 4.997 Å, for O2 and O4 atoms it is 4.937 Å while that across the opposite facing N atoms is 5.494 Å. The benzyl side-arms of the diazacrown are in *syn* conformation with respect to the macrocyclic plane, with the benzylic C atom in each side-arm occupying a flag-pole position and with the phenyl groups

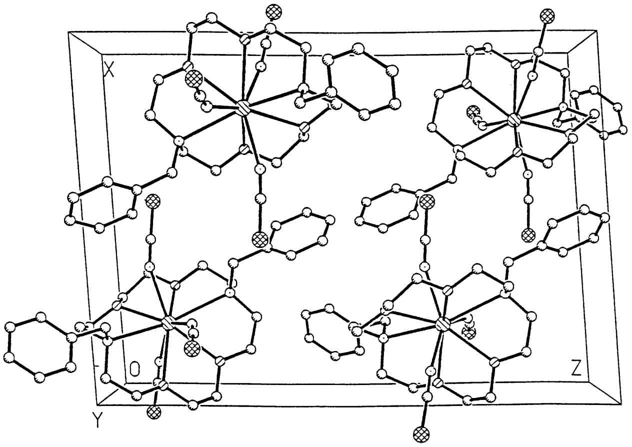

Fig. 3. Unit-cell packing diagram of $La(NCS)_3.C_{26}H_{28}N_2O_4$ viewed along the *Y*-axis.

pointing away from the cavity and not participating in bonding to the La as expected. The thiocyanate ions are bent with the La–N–C bond angles ranging from 139.8 to 166.7°. One of the La–NCS bonds is positioned above the macrocyclic plane while the other two are below and lie in the same direction as the two benzyl substituents.

The torsion angles observed in the complexed macrocyclic ring are nearly equally distributed between *gauche* and *anti* conformations with the following sequence $g^-aag^+aag^-g^-ag^-aag^+aag^-g^-a$ observed (*gauche* is equivalent to synclinal at approximately 60°(g^+) or –60°(g^-); *anti* (*a*) is equivalent to antiperiplanar, at approximately 180° [16]).

The selected geometrical properties of the dibenzyldiazacrown (molecule **2**) in the free state obtained from the semi-empirical PM3 calculation are tabulated in Table 3 and the skeletal structures are shown in Figs. 4a and 4b. The optimisation shows that the free ligand is splayed open and the cavity is elongated with a long-hole distance across the opposite-facing N atoms but shorter distances across the opposite facing O atoms. The free state diazacrown adopts a pseudo D_{2d} symmetry because of the elongation and differs from other diaza-18-crown-6 ligands that adopt the more symmetrical D_{3d} symmetry[17]. It appears that this elongation is the most favoured conformation energetically for the heteroatomic macrocycle with dibenzyl side-arms. Lying approximately in a plane, the O1 and O4 atoms point inwards of the cavity while O2 and O3 point outwards with the N atoms lying above and below this plane to give a chair conformation for the hetero atoms of the macrocycle. Each of the benzyl side-arms attached to the macrocycle is in an equatorial position relative to the mean plane of the macrocycle, and is situated away from the hole, as is expected in the absence of complexation to a cation. The hole size changes upon coordination to La with the O2 to O4 distance shortening from 5.1 to 4.9 Å and the O1 to O3 distance lengthening from 4.7 to 5.0 Å. However the N4 to N5 distance shortens significantly from 9.7 to 5.5 Å upon coordination. These changes reflect the very flexible nature of the macrocycle that enables the macrocycle to curl around La, thereby changing the cavity size considerably upon coordination. Such a structure is similar to the coordination mode and conformations of other

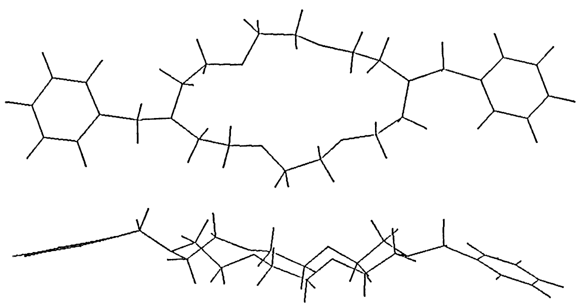

Fig. 4. Views of the skeletal structure of dibenzyldiaza-18-crown-6. (a) top view; (b) side view.

lanthanide 18-crown-6 ligands where the perfect cavity-size–metal-ion-size fit is not realised thereby causing the 18-crown-6 to fold around the metal ion[7]. The PM3 calculation also shows changes in the torsion angles for the free macrocycle which now adopts the $g^{+}aag^{+}aaa\ g^{-}g^{+}g^{-}aag^{+}aaag^{-}g^{-}$ sequence that is different from the coordinated macrocycle above.

4. Conclusion

The X-ray determination shows the three-dimensional configuration of complex 1. The bond distances and bond angles observed are typical for similar complexes. The PM3-calculated bond distances of the free diazacrown are in agreement with the X-ray-generated bond distances for the complexed diazacrown but the bond angles and the torsion angles differ, reflecting the open structure of the free diazacrown compared with the highly constrained structure of the ligating atoms encircling the lanthanum ion. The cavity size of the azacrown changes minimally across the opposite-facing oxygen atoms but decreases markedly across nitrogen upon coordination, demonstrating the highly flexible nature of the diazacrown.

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