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Synthesis and structure of η^6-benzenelanthanoidtris(aluminum tetrachlorides) (Ln = La, Nd, Sm)

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Abstract

The η^6-benzene complexes of lanthanoids $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3 \cdot C_6H_6$ (Ln = La (**1**), Nd (**2**), Sm (**3**)) have been prepared by the reaction of $LnCl_3$ with activated $AlCl_3$ in benzene. The crystal structures of **2** and **3** have been determined. Complexes **2** and **3** each crystallize from benzene in the triclinic space group $P\bar{1}$; with *a* 9.40(2), *b* 9.74(3), *c* 16.61(5) Å, α 96.69(2), β 93.54(3), γ 111.61(2)° for **2**, and *a* 9.46(2), *b* 9.77(3), *c* 16.78(4) Å, α 96.00(2), β 93.7692), γ 111.66(2)° for **3**. The X-ray diffraction study has revealed that the central atom in $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3$-type complexes exerts no distinct influence on the molecular structure. Comparable M–ligand bond lengths reflect the difference in the ionic radii of neodymium and samarium.

Introduction

The first η^6-arene complex of the rare earth element $Sm(\eta^6\text{-}C_6Me_6)(AlCl_4)_3$ (**4**) was prepared by Cotton et al. in 1986 [1]. We have reported the preparation and molecular structure of another complex of this type, $Sm(\eta^6\text{-}m\text{-}(CH_3)_2C_6H_4)(AlCl_4)_3$ (**5**) [2]. These results indicate unambiguously that samarium can form a stable π bond with a neutral arene ligand.

Cotton et al. have pointed out that a $SmCl_3$ solution changes colour from yellow to blood-red when treated with $AlCl_3$, Al foil, and hexamethylbenzene in refluxing toluene [1]. We observed the same phenomenon during the preparation of **5**. It seems that the reduction is required for the formation of the η^6-arene samarium complex, because the blood-red color of the solution is indicative of Sm^{II} compounds. In general, early lanthanoid elements are difficult to reduce, and we wondered whether samarium is a special case. Thus, we extended our studies to

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include the synthesis of this type of complex of the early lanthanoids. Here we report the synthesis of $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3 \cdot C_6H_6$, where Ln = La (**1**), Nd (**2**), and Sm (**3**). The structures of **2** and **3** have been determined.

Results and discussion

Synthesis

$LnCl_3$ (Ln = La, Nd, Sm) reacts with benzene under reducing, Friedel–Crafts conditions to give the η^6-benzene complexes **1**, **2**, or **3**. These complexes are very sensitive to air and moisture. IR spectra of **1**, **2** and **3** are similar, in that all show the bands that can be attributed to the various modes of the benzene ring. The absorption bands of **3** are as follows: 3070(s), 1920(m), 1610(s), 1470(s), 1440(s), 1020(s), 880(m) cm^{-1}.

As in the case of Sm, a distinct change from white to yellow of the La solution and one from purple to dark red of the Nd solution was observed during the reaction; a tarry residue was formed in addition to the desired product. As the paths by which the three complexes are formed must be the same, the reduction of Nd^{III} and La^{III} must have occurred under the reaction conditions.

Structure

The η^6-benzene complexes **2** and **3** are isomorphous and isostructural. A perspective drawing of the molecular structure is shown in Fig. 1. The atom numbering scheme pertains to both complexes. Important bond lengths and bond angles are listed in Tables 1 and 2, respectively. The molecular structures of the two complexes

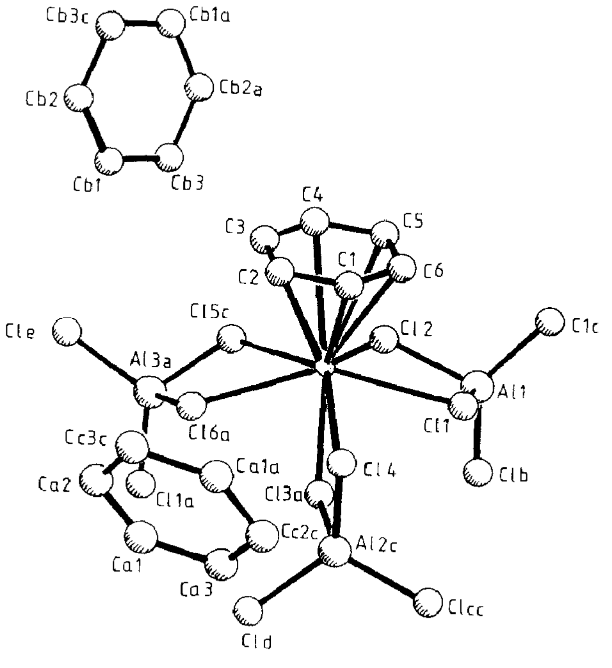

Fig. 1. The structure of $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (Ln = Nd (**2**), Sm (**3**), the atom numbering scheme pertains to both **2** and **3**.

Table 1

Selected bond lengths (Å) and bond angles (°) for complex **2**

Nd–C(1)	2.94(2)	Nd–Cl(3)	2.795(8)	Al(2)–Cl(3)	2.221(9)
Nd–C(2)	2.93(2)	Nd–Cl(4)	2.845(6)	Al(2)–Cl(4)	2.19(1)
Nd–C(3)	2.93(2)	Nd–Cl(5)	2.861(5)	Al(2)–Clc	2.08(1)
Nd–C(4)	2.93(2)	Nd–Cl(6)	2.885(6)	Al(2)–Cld	2.10(1)
Nd–C(5)	2.93(2)	Al(1)–Cl(1)	2.191(9)	Al(3)–Cl(5)	2.18(1)
Nd–C(6)	2.94(2)	Al(1)–Cl(2)	2.21(1)	Al(3)–Cl(6)	2.183(8)
Nd–Cl(1)	2.883(7)	Al(1)–Cla	2.08(1)	Al(3)–Cle	2.12(6)
Nd–Cl(2)	2.842(6)	Al(1)–Clb	2.09(1)	Al(3)–Clf	2.09(1)
Cl(1)–Nd–Cl(2)	69.8(2)	Cl(3)–Nd–C(3)	151.9(3)		
Cl(1)–Nd–Cl(3)	80.1(2)	Cl(3)–Nd–C(4)	156.8(3)		
Cl(1)–Nd–Cl(4)	73.2(2)	Cl(3)–Nd–C(5)	155.8(4)		
Cl(1)–Nd–Cl(5)	136.3(2)	Cl(3)–Nd–C(6)	150.3(3)		
Cl(1)–Nd–Cl(6)	144.2(2)	Cl(4)–Nd–Cl(5)	137.5(2)		
Cl(1)–Nd–C(1)	88.6(3)	Cl(4)–Nd–Cl(6)	72.6(2)		
Cl(1)–Nd–C(2)	116.0(3)	Cl(4)–Nd–C(1)	72.8(4)		
Cl(1)–Nd–C(3)	128.0(3)	Cl(4)–Nd–C(2)	83.6(4)		
Cl(1)–Nd–C(4)	109.0(3)	Cl(4)–Nd–C(3)	110.7(4)		
Cl(1)–Nd–C(5)	82.1(3)	Cl(4)–Nd–C(4)	129.2(4)		
Cl(1)–Nd–C(6)	71.8(3)	Cl(4)–Nd–C(5)	116.5(3)		
Cl(2)–Nd–Cl(3)	83.7(2)	Cl(4)–Nd–C(6)	89.0(4)		
Cl(2)–Nd–Cl(4)	139.2(2)	Cl(5)–Nd–Cl(6)	69.3(2)		
Cl(2)–Nd–Cl(5)	68.8(2)	Cl(5)–Nd–C(1)	125.4(3)		
Cl(2)–Nd–Cl(6)	136.6(2)	Cl(5)–Nd–C(2)	100.3(3)		
Cl(2)–Nd–C(1)	122.1(4)	Cl(5)–Nd–C(3)	76.8(3)		
Cl(2)–Nd–C(2)	128.2(4)	Cl(5)–Nd–C(4)	76.7(3)		
Cl(2)–Nd–C(3)	105.4(4)	Cl(5)–Nd–C(5)	99.9(3)		
Cl(2)–Nd–C(4)	79.9(4)	Cl(5)–Nd–C(6)	125.2(3)		
Cl(2)–Nd–C(5)	74.9(4)	Cl(6)–Nd–C(1)	91.3(3)		
Cl(2)–Nd–C(6)	95.3(4)	Cl(6)–Nd–C(2)	70.1(3)		
Cl(3)–Nd–Cl(4)	73.5(2)	Cl(6)–Nd–C(3)	74.9(4)		
Cl(3)–Nd–Cl(5)	82.1(2)	Cl(6)–Nd–C(4)	100.6(3)		
Cl(3)–Nd–Cl(6)	80.3(2)	Cl(6)–Nd–C(5)	123.2(4)		
Cl(3)–Nd–C(1)	146.3(4)	Cl(6)–Nd–C(6)	117.8(4)		
Cl(3)–Nd–C(2)	147.0(4)				

are nearly the same as the structures of **4** [3] and $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ [4]. The coordination polyhedra of the metal centers are approximately pentagonal bipyramids. Five chlorine atoms (Cl(1), Cl(2), Cl(4), Cl(5) and Cl(6)) bonded to the central metal atom are located in a plane having deviations of 0.004 to 0.089 Å for Nd, and of 0.098 to 0.175 Å for Sm. The Cl–M–Cl bond angles for adjacent chlorine atoms in the plane range from 68.8° to 73.2° for Nd and from 68.9 to 73.4° for Sm, which are somewhat larger than those found in **4** (69.4° to 71.1°) [1]. The sixth chlorine atom (Cl(3)) occupies the one apical position and the benzene molecule occupies the other.

The mean distances of $M\text{–}Cl^p$ (chlorine in the plane) and $M\text{–}Cl^a$ (chlorine in the apical position) are 2.86(6) Å ($Nd\text{–}Cl^p$), 2.84(1) Å ($Sm\text{–}Cl^p$) and 2.79(8) Å ($Nd\text{–}Cl^a$), 2.77(1) Å ($Sm\text{–}Cl^a$). There are no obvious differences between the bond distances of Sm–Cl and Nd–Cl, if the differences in ionic radii of Nd^{III} and Sm^{III} 0.031 Å, is considered. The average distances $Nd\text{–}Cl^p$, $Sm\text{–}Cl^p$ and $Nd\text{–}Cl^a$, $Sm\text{–}Cl^a$ are also comparable to the analogous distances in $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$,

Table 2

Selected bond lengths (Å) and bond angles (°) for complex **3**

Sm–C(1)	2.927(6)	Sm–Cl(5)	2.845(1)	C(1)–C(2)	1.372(7)
Sm–C(2)	2.910(7)	Sm–Cl(6)	2.865(1)	C(2)–C(3)	1.366(8)
Sm–C(3)	2.898(7)	Al(1)–Cl(1)	2.184(2)	C(3)–C(4)	1.359(9)
Sm–C(4)	2.895(8)	Al(1)–Cl(2)	2.185(2)	C(4)–C(5)	1.43(1)
Sm–C(5)	2.910(8)	Al(1)–Cla	2.064(2)	C(5)–C(6)	1.40(1)
Sm–C(6)	2.912(6)	Al(1)–Clb	2.080(3)	C(6)–C(1)	1.39(1)
Sm–Cl(1)	2.865(1)	Al(2)–Cl(3)	2.200(2)	Al(3)–Cl(5)	2.191(2)
Sm–Cl(2)	2.817(1)	Al(2)–Cl(4)	2.182(2)	Al(3)–Cl(6)	2.191(2)
Sm–Cl(3)	2.772(1)	Al(2)–Clc	2.081(2)	Al(3)–Cle	2.085(2)
Sm–Cl(4)	2.811(1)	Al(2)–Cld	2.091(2)	Al(3)–Clf	2.082(2)
Cl(1)–Sm–Cl(2)	69.8(1)	Cl(3)–Sm–C(6)	148.4(1)		
Cl(1)–Sm–Cl(3)	79.6(1)	Cl(4)–Sm–Cl(5)	137.6(1)		
Cl(1)–Sm–Cl(4)	73.4(1)	Cl(4)–Sm–Cl(6)	72.2(1)		
Cl(1)–Sm–Cl(5)	136.6(1)	Cl(4)–Sm–C(1)	72.2(1)		
Cl(1)–Sm–Cl(6)	144.0(1)	Cl(4)–Sm–C(2)	83.3(1)		
Cl(1)–Sm–C(1)	88.0(1)	Cl(4)–Sm–C(3)	110.0(1)		
Cl(1)–Sm–C(2)	115.1(1)	Cl(4)–Sm–C(4)	128.6(1)		
Cl(1)–Sm–C(3)	126.7(1)	Cl(4)–Sm–C(5)	115.8(1)		
Cl(1)–Sm–C(4)	108.6(1)	Cl(4)–Sm–C(6)	88.0(2)		
Cl(1)–Sm–C(5)	80.5(2)	Cl(5)–Sm–Cl(6)	69.5(2)		
Cl(1)–Sm–C(6)	70.6(1)	Cl(5)–Sm–C(1)	125.7(1)		
Cl(2)–Sm–Cl(3)	83.1(1)	Cl(5)–Sm–C(2)	100.6(1)		
Cl(2)–Sm–Cl(4)	139.1(1)	Cl(5)–Sm–C(3)	77.6(1)		
Cl(2)–Sm–Cl(5)	68.9(1)	Cl(5)–Sm–C(4)	77.0(1)		
Cl(2)–Sm–Cl(6)	136.8(1)	Cl(5)–Sm–C(5)	100.8(1)		
Cl(2)–Sm–C(1)	122.5(1)	Cl(5)–Sm–C(6)	126.2(2)		
Cl(2)–Sm–C(2)	128.4(1)	Cl(6)–Sm–C(1)	91.3(1)		
Cl(2)–Sm–C(3)	105.8(1)	Cl(6)–Sm–C(2)	70.8(1)		
Cl(2)–Sm–C(4)	80.6(1)	Cl(6)–Sm–C(3)	75.8(1)		
Cl(2)–Sm–C(5)	74.8(2)	Cl(6)–Sm–C(4)	100.9(1)		
Cl(2)–Sm–C(6)	95.8(2)	Cl(6)–Sm–C(5)	124.5(2)		
Cl(3)–Sm–Cl(4)	73.4(1)	Cl(6)–Sm–C(6)	118.1(2)		
Cl(3)–Sm–Cl(5)	83.0(1)	Cl(1)–Al(1)–Cl(2)	96.2(1)		
Cl(3)–Sm–Cl(6)	80.9(1)	Cl(3)–Al(2)–Cl(4)	99.2(1)		
Cl(3)–Sm–C(1)	145.5(1)	Cl(5)–Al(3)–Cl(6)	96.0(1)		
Cl(3)–Sm–C(2)	147.7(1)	Cla–Al(1)–Clb	116.0(1)		
Cl(3)–Sm–C(3)	153.7(1)	Clc–Al(2)–Cld	116.7(1)		
Cl(3)–Sm–C(4)	157.7(1)	Cle–Al(3)–Clf	116.9(1)		
Cl(3)–Sm–C(5)	154.2(1)				

2.89(7) Å (U–Cl^p) and 2.84(7) Å (U–Cl^a) [4] as U^{III} is approximately 0.30 and 0.61 Å larger than Nd^{III} and Sm^{III}, respectively. The metal atoms are substantially displaced by 0.5 Å for Nd and 0.5 Å for Sm from the plane toward the benzene ring. The values are approximately the same as that in $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ (nearly 0.5 Å) [4] but are much smaller than that in **4**, 0.63 Å [1], probably because the interaction between the methyl groups of hexamethylbenzene and Cl^p atoms is larger than the interaction between hydrogen atoms of benzene and the Cl^p atoms. The Sm–C distance, average 2.91(6) Å, is shorter than the Nd–C distance, 2.93(3) Å. This is because of lanthanoid contraction.

We can see from the above discussion that the central atom in $Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ exerts no distinct influence on molecular structure. The interaction between the arene ligand and the equatorial chlorine atoms is the main factor affecting the fine structure of this type of complexes.

Experimental

Operations, synthetic techniques, materials and instruments are as described previously [2].

$Ln(\eta^6\text{-}C_6H_6)(AlCl_4)_3 \cdot C_6H_6$

In a typical procedure, 3 mmol of $AlCl_3$ and an excess of aluminum powder were heated together at 130–140 °C for 40 min, then 1 mmol of $LnCl_3$ (Ln = La, Nd, Sm) and 30 ml of benzene were added. The mixture was stirred at 80 °C until a distinct color change occurred. After centrifugation the solution was concentrated and crystallized at room temperature. A dark tar in the case of La and Nd, and a red tar in the case of Sm was observed at the bottom of the flask several days later. After the tar was removed, the complex was crystallized from benzene solution at room temperature. Crystals separated during several days. Yield: **1**, 450 mg (56%); **2**, 500 mg (62%); **3**, 310 mg (38%). Anal. Found: **1**, La, 18.06; Cl, 52.78%. **2**, Nd, 18.16; Cl, 53.76%. **3**, Sm, 18.42; Cl, 51.95%. $C_{12}H_{12}Cl_{12}Al_3In$ calcd.: **1**, La, 17.32; Cl, 53.12%. **2**, Nd, 17.80; Cl, 52.79%. **3**, Sm, 18.49; Cl, 52.37%.

Table 3

Information for data collection and refinement of arene complexes **2** and **3**

	2	**3**
Formula	$C_{12}H_{12}Cl_{12}Al_3Nd$	$C_{12}H_{12}Cl_{12}Al_3Sm$
Fw	806.9	813.0
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.397(3)	9.456(2)
b (Å)	9.739(3)	9.765(3)
c (Å)	16.612(5)	16.776(4)
α (°)	96.69(2)	96.00(2)
β (°)	93.54(3)	93.76(2)
γ (°)	111.61(2)	111.66(2)
V (Å^3)	1394.7(7)	1422.6(5)
Z	2	2
D_c (g cm^{-3})	1.92	1.90
Crystal size (mm)	0.2×0.2×0.2	0.2×0.2×0.2
μ(MoK_α), (cm^{-1})	31.15	16.60
Temperature (°C)	−60	23
Scan method	–	–
R [a]	0.070	0.031
R_w [b]	0.078	0.031
Data collection:		
Range (2θ), deg	3–46	3–60
No. of unique data	5334	7335
Total with $F_o^2 > 3\sigma(F_o^2)$	3283	5343

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

X-ray crystallography

All geometrical and intensity data were obtained by an R3M/E automated four-circle diffractometer.

Structure of **2**

A suitable crystal was inspected under a microscope and was protected by a stream of nitrogen during X-ray work. The data were corrected for *LP* factors but not for absorption. The heavy atom position was derived from a three-dimensional Patterson map. All the non-hydrogen atoms, including six of the carbon atoms of the two solvent (benzene) molecules, were determined by Fourier technique. Three of the six carbon atoms make up a semi-benzene ring. They are both located around a center of inversion, so that the other three carbon atoms in the ring were generated by an inversion operation. The refinement converged at residuals $R = 0.078$, $R_w = 0.070$. Details of the data collection and refinement are listed in Table 3. Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 4.

Table 4

Atomic coordinates ($\times 10^4$) for complex **2**

	x	y	z	U_{eq}
Nd	5352(2)	976(2)	2622(1)	27(1)
Cl(1)	8605(9)	2624(7)	2516(3)	40(3)
Cl(2)	6132(8)	926(7)	896(3)	34(3)
Cl(3)	6420(8)	−1348(6)	2534(3)	32(3)
Cl(4)	6760(8)	1274(7)	4133(3)	36(3)
Cl(5)	2921(8)	−1244(7)	1416(4)	35(3)
Cl(6)	3073(8)	−968(7)	3401(3)	36(3)
Cla	9637(8)	3624(8)	573(4)	55(4)
Clb	9518(10)	178(8)	1093(4)	54(4)
Clc	9837(10)	91(8)	3897(4)	55(4)
Cld	6297(11)	−2354(8)	4479(4)	56(4)
Cle	−0527(9)	−3100(7)	2225(4)	46(3)
Clf	2553(10)	−4427(7)	2341(4)	47(3)
Al(1)	8654(10)	1878(8)	1225(4)	32(3)
Al(2)	7646(10)	−629(8)	3827(4)	36(4)
Al(3)	1871(10)	−2615(8)	2334(4)	35(3)
C(1)	5162(16)	3644(16)	3457(11)	36(9)
C(2)	3641(16)	2620(16)	3328(11)	76(23)
C(3)	2883(16)	2131(16)	2538(11)	34(10)
C(4)	3645(16)	2666(16)	1877(11)	37(9)
C(5)	5166(16)	3691(16)	2006(11)	62(14)
C(6)	5925(16)	4180(16)	2796(11)	63(13)
Ca(1)	4563(46)	3537(32)	9614(14)	61(17)
Ca(2)	13461(34)	4004(30)	9807(15)	44(11)
Ca(3)	16192(40)	4519(31)	9822(15)	53(15)
Cb(1)	10137(61)	3997(36)	5459(24)	75(19)
Cb(2)	9176(73)	4704(50)	5640(22)	119(32)
Cb(3)	11037(61)	4260(44)	4878(25)	90(24)

Table 5

Atomic coordinates ($\times 10^4$) for complex 3

	x	y	z	U_{eq}
Sm	5294(1)	947(1)	2519(1)	38(1)
Cl(1)	8508(1)	2567(1)	2511(1)	59(1)
Cl(2)	6072(1)	881(2)	927(1)	61(1)
Cl(3)	3634(1)	1337(1)	7449(1)	51(1)
Cl(4)	6663(1)	1230(1)	4099(1)	56(1)
Cl(5)	7124(1)	1229(1)	8559(1)	58(1)
Cl(6)	6954(1)	949(1)	6601(1)	54(1)
Cla	9460(2)	3665(2)	608(1)	103(1)
Clb	9474(2)	252(2)	1095(1)	97(1)
Clc	−261(2)	75(2)	3901(1)	85(1)
Cld	3754(2)	2357(2)	5522(1)	93(1)
Cle	−537(1)	−3035(2)	2260(1)	78(1)
Clf	7557(2)	4423(2)	7637(1)	79(1)
Al(1)	8553(2)	1885(2)	1234(1)	54(1)
Al(2)	2635(2)	644(2)	6181(1)	54(1)
Al(3)	8198(2)	2600(2)	7646(1)	53(1)
C(1)	5153(7)	3609(6)	3433(4)	80(3)
C(2)	3659(6)	2626(6)	3298(4)	70(3)
C(3)	2926(6)	2167(6)	2532(4)	69(2)
C(4)	3651(8)	2655(7)	1884(4)	88(3)
C(5)	5215(10)	3672(7)	1997(5)	105(4)
C(6)	5942(8)	4126(6)	2786(6)	99(4)
Ca(1)	4543(10)	3616(7)	9588(4)	110(4)
Ca(2)	3471(8)	4115(8)	9822(4)	106(4)
Ca(3)	6063(9)	4486(9)	9758(4)	117(5)
Cb(1)	79(17)	3932(11)	5424(8)	135(6)
Cb(2)	−886(14)	4628(16)	5591(6)	144(6)
Cb(3)	979(11)	4314(13)	4859(9)	124(5)

Structure of 3

The crystal for X-ray work was sealed in a Lindemann glass capillary glass under argon. The intensities were corrected for *LP* factors and for absorption. The Sm atom was located by Patterson technique. Light atoms were derived on successive Fourier synthesis. The benzene molecules of crystallization in the lattice were treated as in the structure of **2**. All positional parameters and temperature factors for non-hydrogen atoms were refined anisotropically. The crystal and data collection details are given in Table 3. Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 5.

Supplementary material available. A full list of bond distances and bond angles (6 pages); tables of anisotropic thermal parameters (4 pages), and listings of observed and calculated structure factors (30 pages) are available from the authors.

Acknowledgement

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