

# Bis(tetramethylcyclopentadienyl)gallium(III) chloride, tris(tetramethylcyclopentadienyl)gallium(III) and tris(pentamethylcyclopentadienyl)gallium(III)

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## Abstract

(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>GaCl (1) and Ga(C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub> (2) have been prepared from GaCl<sub>3</sub> and NaC<sub>5</sub>Me<sub>4</sub>H, whereas Ga(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub> (3) was made from GaCl<sub>3</sub> and KC<sub>5</sub>Me<sub>5</sub>. Compounds 1–3 were characterized by elemental analyses, mass spectra, nuclear magnetic resonance and vapour pressure measurements and 3 by an X-ray structural study. The compounds are colourless, crystalline solids and dissolve in ether, pentane and benzene. Compounds 1 and 2 slowly decompose at room temperature under inert gas while 3 is stable and can be exposed to air for short periods of time in the solid state. Compound 3 crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 1579.0(3) pm, *b* = 1203.9(3) pm, *c* = 1599.1(4) pm,  $\beta$  = 117.40(1)° and *d*<sub>calc</sub> = 1.17 g cm<sup>-3</sup> for *Z* = 4. Full-matrix least-squares refinement gave an *R* value of 0.046 for 3469 observed reflections. Crystalline 3 consists of discrete molecules with all C<sub>5</sub>Me<sub>5</sub> rings  $\eta^1$  bonded to Ga with an average C–Ga distance of 203.7 pm. The immediate environment of gallium is planar within 0.29 ± 0.09 pm.

**Key words:** Gallium; Metallocenes; Cyclopentadienyl; MOCVD; X-ray diffraction; Crystal structure

## 1. Introduction

Trivalent Group III metallocenes are potentially useful as volatile materials for metal–organic chemical vapour deposition (MOCVD) of Group III–V (13–15) semiconducting materials; tris(cyclopentadienyl)gallium has recently been used successfully in MOCVD [1]. Our knowledge of this class of compounds, however, is rather limited. The only structurally characterized compounds that have been reported are tris(cyclopentadienyl)gallium(III) [2], bis(pentamethylcyclopentadienyl)gallium(III) chloride [3], pentamethylcyclopentadienyl-gallium(III) dichloride [3] and tris(cyclopentadienyl)indium(III) [4]. As a part of our programme to develop suitable precursors for the preparation of III–V semiconducting materials the syntheses and properties of bis(tetramethylcyclopentadienyl)gallium(III) chloride (1), tris(tetramethylcyclopentadienyl)gallium

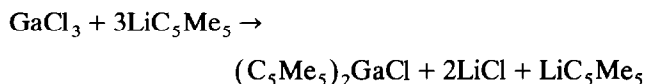
(III) (2), and tris(pentamethylcyclopentadienyl)gallium(III) (3) have been investigated.

## 2. Syntheses and properties

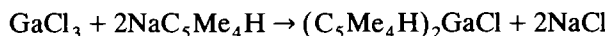
Previous reports have shown that the choice of the metal in alkali cyclopentadienides affects the outcome of salt elimination reactions that yield Group III cyclopentadienides. Reaction of indium(III) chloride with sodium cyclopentadienide gives tris(cyclopentadienyl)indium(III) only in trace quantities, together with cyclopentadienylindium(I) [5], while the corresponding reaction with LiC<sub>5</sub>H<sub>5</sub> gives the indium(III) compound as the main product [6]. The latter exists as a polymeric compound containing both bridging and  $\eta^1$ - $\sigma$ -bonded rings [3]. Ga(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub> has been prepared in the same manner, and an X-ray structural study shows that it is present in the crystal as discrete molecules. The compound displays weak Lewis-acid behaviour, readily forming adducts with ether, tetrahydrofuran (THF) and methyl amine [4]. Its <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra have been studied but are

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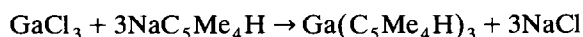
not very informative [3,7]. Surprisingly the analogous reaction of  $GaCl_3$  with a three-molar proportion of  $LiC_5Me_5$  stops at  $(C_5Me_5)_2GaCl$  and does not give the homoleptic compound  $Ga(C_5Me_5)_3$  [2]:



We decided to try to use sodium or potassium cyclopentadienides, which have been used successfully in the preparation of alkylgalliumcyclopentadienides [8]. We found that the reaction of  $GaCl_3$  with  $NaC_5Me_4H$  in ether can be directed to give either  $(C_5Me_4H)_2GaCl$  (1) or  $Ga(C_5Me_4H)_3$  (2) with reasonable yields:

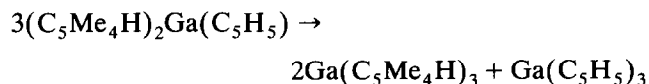
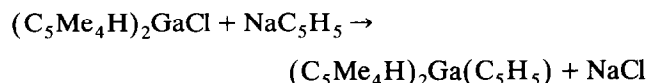


1



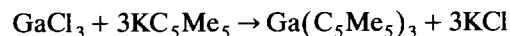
2

The white crystalline compounds undergo slow decomposition at room temperature under argon.  $(C_5Me_4H)_2GaCl$  (1) is of particular interest as a possible starting material for the synthesis of other trial precursors for III–V semiconductors via chloride substitution; for example, alkyl bis(cyclopentadienyl)gallium compounds  $(C_5Me_4H)_2GaR$  or bis(cyclopentadienyl)gallium hydride. Our first attempts to make  $(C_5Me_4H)_2Ga(C_5H_5)$  by this route, however, were unsuccessful.  $Ga(C_5Me_4H)_3$  was isolated and mass spectral evidence was obtained for the presence of  $Ga(C_5H_5)_3$  in the precipitate:



The reaction may involve the intermediate  $(C_5Me_4H)_2Ga(C_5H_5)$  and it is being further investigated.

Gallium trichloride reacts with  $KC_5Me_5$  in ether to give  $Ga(C_5Me_5)_3$  (3), which crystallizes readily as colourless needles.



3

It does not form adducts with ether or tetrahydrofuran.

Compound 3 does not decompose at room temperature under an inert gas, but when it is exposed to air, a yellow protective film develops on the surface of the crystals. Pure material can be recovered from partly decomposed samples by recrystallization from ether.

The three new compounds 1–3 have been characterized by elemental analyses and mass spectroscopy (MS). In addition,  $Ga(C_5Me_5)_3$  (3), as the first homoleptic gallium compound containing a substituted cyclopentadienide, has been investigated further by  $^1H$  NMR,  $^{13}C$  NMR, X-ray crystallography and vapour pressure measurements. Compound 3 is thermally stable and can be stored at room temperature, whereas the tetramethylcyclopentadienide derivatives 1 and 2 are thermally unstable and decompose slowly at room temperature. The best method of isolating them in a pure state is by rapid concentration of the reaction solution and subsequent cooling to  $-30^\circ C$  for crystallization. In contrast with  $Ga(C_5H_5)_3$ , both  $Ga(C_5Me_4H)_3$  (2) and  $Ga(C_5Me_5)_3$  (3) separate out from ether or THF as solvent-free compounds and can be further purified by recrystallization from the same solvents. The 70 eV mass spectra of 1–3 are dominated by the  $[M-(C_5Me_5)]^+$  or  $[M-(C_5Me_4H)]^+$  ions and display only small molecular ions, with intensities of less than 3% of the base peak. The  $^1H$  NMR spectrum of 3 in hexadeuterobenzene shows only one singlet for the methyl groups, indicating a rapid rotation of the ring in solution, as do the unique signals for the ring carbons and for the methyl carbon atoms in the  $^{13}C$  NMR spectrum. Neither spectrum gives any indication of the presence of coordinated solvent. In the  $^1H$  NMR spectra of 1 and 2 the resonance for the ring protons appears at 2.62 and 2.53 ppm, indicating  $\eta^1$  bonding between the carbon ring and the gallium centre.

Compound 3 exhibits an unexpectedly high vapour pressure of 130 Pa at  $12.5^\circ C$ . Vapour pressures were recorded at temperatures between  $-10$  and  $+12.5^\circ C$  and were found to show the relationship  $\log p = 5.851 - 1066.81/T$ , with a vapourization enthalpy  $\Delta H^{lv} = 20.423 \text{ kJ mol}^{-1}$ . A plot of  $\log p$  against  $1/T$  is shown in Fig. 1.

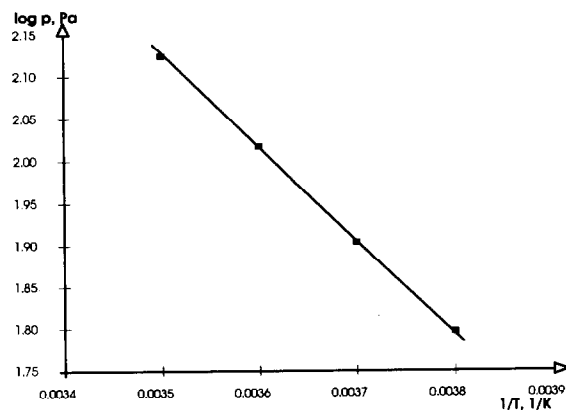


Fig. 1. Vapour pressure of  $Ga(C_5Me_5)_3$  (3) as a function of temperature.

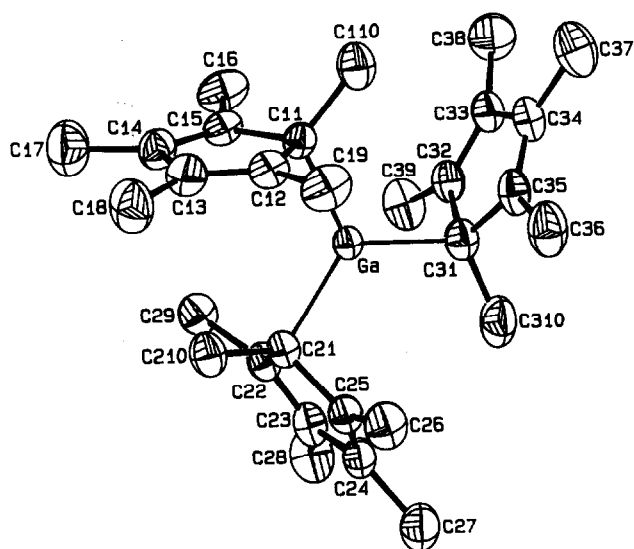


Fig. 2. ORTEP [9] projection of one molecule of  $Ga(C_5Me_5)_3$  (**3**) with the numbering scheme. Hydrogen atoms are excluded for clarity.

### 3. Crystal and molecular structure of $Ga(C_5Me_5)_3$ (**3**)

The X-ray structure of  $Ga(C_5Me_5)_3$  (**3**) shows the Ga atom to be in a slightly distorted trigonal planar environment, with the three bonded carbon atoms C(11), C(21) and C(31) at distances of 204 pm, 203 pm and 204 pm respectively (Fig. 2). Bond distances for **3** are given in Table 1 and bond angles in Table 2. By comparison, in  $Ga(C_5H_5)_3$  the average Ga–C bond distance is 205 pm [4]. Using a mean-planes fit the Ga atom is shown to lie  $0.29 \pm 0.09$  pm below the plane of C(11), C(21) and C(31). The three  $C_5Me_5$  rings are planar, with two of them perpendicular to the C(11)–C(21)–C(31) plane and the third at  $87 \pm 1^\circ$ , thus preventing the molecule from having a threefold axis of symmetry. In the crystal the molecules are at normal van der Waals distances and are arranged in long chains in a staggered manner forming isolated triangular strings.

TABLE 1. Selected bond distances in  $Ga(C_5Me_5)_3$  (**3**) (estimated standard deviations in the last significant figures are given in parentheses)

Bond distance (pm)		Bond distance (pm)	
Ga–C(11)	204.0(4)	C(12)–C(19)	151.3(6)
Ga–C(21)	203.2(4)	C(13)–C(14)	145.5(6)
Ga–C(31)	204.1(4)	C(13)–C(18)	150.3(6)
C(11)–C(12)	147.8(6)	C(14)–C(15)	135.5(6)
C(11)–C(15)	148.8(6)	C(14)–C(17)	150.3(6)
C(11)–C(110)	153.8(6)	C(15)–C(16)	149.5(6)
C(12)–C(13)	133.8(6)		

TABLE 2. Selected bond angles in  $Ga(C_5Me_5)_3$  (**3**) (estimated standard deviations in the last significant figures are given in parentheses)

Bond angle (°)		Bond angle (°)	
C(11)–Ga–C(21)	120.9(2)	C(11)–C(12)–C(13)	109.6(4)
C(11)–Ga–C(31)	120.0(2)	C(12)–C(13)–C(14)	109.0(4)
C(21)–Ga–C(31)	119.1(2)	C(13)–C(14)–C(15)	109.1(4)
Ga–C(11)–C(12)	103.3(3)	C(14)–C(15)–C(11)	108.4(4)
Ga–C(11)–C(55)	102.0(3)	C(15)–C(11)–C(12)	103.8(3)
Ga–C(21)–C(22)	103.2(3)	Ga–C(11)–C(110)	117.0(3)
Ga–C(21)–C(25)	105.3(3)	C(12)–C(11)–C(110)	114.5(4)
Ga–C(31)–C(32)	101.9(3)	C(11)–C(12)–C(19)	122.2(4)
Ga–C(31)–C(35)	105.3(3)	C(12)–C(13)–C(18)	126.9(5)

## 4. Experimental details

### 4.1. General comments

All the compounds used were very sensitive to oxygen and moisture and were manipulated under dry oxygen-free argon. All solvents were dried over sodium and benzophenone and distilled prior to use. Gallium trichloride was prepared from Ga and  $Cl_2$  and freshly sublimed prior to use. Tetramethylcyclopentadienyl sodium was prepared from tetramethylcyclopentadiene

TABLE 3. Crystal and data collection parameters for  $Ga(C_5Me_5)_3$  (**3**)

Formula	$C_{30}H_{45}Ga$
Molecular weight (g mol <sup>-1</sup> )	475.41
Crystal system	Monoclinic
Space group	$P2_1/n$ (non-standard No. 14)
Crystal dimensions (mm × mm × mm)	0.33 × 0.40 × 0.33
<i>a</i> (pm)	1579.0(3)
<i>b</i> (pm)	1203.9(3)
<i>c</i> (pm)	1599.1(4)
$\beta$ (°)	117.40(1)
<i>V</i> (× 10 <sup>6</sup> pm <sup>3</sup> )	2699(1)
<i>Z</i>	4
$\rho_{calc}$ (g cm <sup>-3</sup> )	1.17
$\mu_{calc}$ (cm <sup>-1</sup> )	10.27
<i>F</i> (000)	1024
Radiation	Mo $K_\alpha$ ( $\lambda = 71.069$ Å)
Monochromator	Graphite crystal
Temperature (K)	160(5)
Scan range	$4^\circ \leq 2\theta \leq 50^\circ$ (0 → 18, 0 → 14, –19 → 19)
Scan width (°)	$0.88 + 0.35 \tan \theta$
Aperture (mm)	2.5
Number of reflections measured	5153
Number of unique reflections	4380 ( $R_{int} = 0.0192$ )
Observed reflections	3469, $F_o \geq 4\sigma(F_o)$
Number of parameters varied	280
Maximum shift/error $\Delta/\sigma$	0.001
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.046
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o^2]^{1/2}$	0.049, $w = 1/\sigma^2(F_o)$

and sodium amide in THF, cyclopentadienylsodium from commercially available cyclopentadiene and sodium in THF, and pentamethylcyclopentadienyl potassium from pentamethylcyclopentadiene [10] and potassium in THF. Elemental analyses were performed on a Perkin–Elmer Series II CHNS/O analyser 2400, NMR data were recorded on a Bruker WH270 in sealed tubes with  $C_6D_6$  as solvent, and mass spectra were recorded as electron impact (EI) spectra on a Varian MAT 311A. The vapour pressures were determined by expansion of the vapour into an evacuated flask and measurement of the equilibrium pressure with a baratron. Samples of the vapour were analysed in a connected quadrupole mass spectrometer.

#### 4.2. Bis(tetramethylcyclopentadienyl)gallium(III) chloride (1)

In a 250 ml Schlenk tube,  $GaCl_3$  (2.77 g, 15.7 mmol) was dissolved in 80 ml of diethyl ether at  $-78^\circ C$ , and 17.25 ml of a 1.82 M solution of  $NaC_5Me_4H$  (31.4 mmol) in THF were added with stirring. The mixture

was allowed to warm to room temperature and stirred for an additional 12 h; then the yellow solution was filtered through a D4-sintered glass frit to leave a white precipitate. The clear solution was kept at  $-30^\circ C$  for 24 h to yield colourless needles of **1**. Concentration of the remaining solution yielded a second crop. The total yield was 4.48 g (82%). Anal. Found: C, 63.17; H, 7.79; Cl, 9.90.  $C_{18}H_{26}ClGa$  (**1**) calcd: C, 62.20; H, 7.54; Cl, 10.20%,  $^1H$  NMR ( $C_6D_6$ ,  $25^\circ C$ , 270 MHz): 1.61 (s, 12H,  $CH_3$ ); 1.72 (s, 12H,  $CH_3$ ); 2.62 (s, 2H, CH) ppm. MS (70 eV, EI):  $m/z$  346 ( $[M]^+$ ).

#### 4.3. Tris(tetramethylcyclopentadienyl)gallium(III) (2)

(a) A cold ( $-78^\circ C$ ), magnetically stirred solution of  $GaCl_3$  (1.89 g, 10.79 mmol) in 80 ml of diethyl ether was treated with 4.66 g (32.37 mmol) of dry  $NaC_5Me_4H$ . Subsequent procedures as described for the preparation of **1** gave 3.69 g (79%) of colourless needles of **2** which were isolated in two crops. Anal. Found: C, 73.64; H, 8.90,  $C_{27}H_{39}Ga$  (**2**) calcd: C, 74.96; H, 9.09%.  $^1H$  NMR ( $C_6D_6$ ,  $25^\circ C$ , 270 MHz): 1.51 (s, 12H,  $CH_3$ );

TABLE 4. Fractional atomic coordinates and thermal parameters for  $Ga(C_5Me_5)_3$  (with estimated standard deviations)

Atom	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
Ga	0.24038(3)	0.23800(3)	0.02589(3)	1.82
C(11)	0.3152(3)	0.2855(3)	-0.0435(3)	2.19
C(12)	0.3859(3)	0.3649(4)	0.0223(3)	2.61
C(13)	0.3598(3)	0.4686(4)	-0.0090(3)	3.13
C(14)	0.2720(3)	0.4648(4)	-0.0973(3)	2.90
C(15)	0.2450(3)	0.3575(4)	-0.1195(3)	2.41
C(16)	0.1648(3)	0.3124(5)	-0.2073(3)	3.75
C(17)	0.2229(4)	0.5673(5)	-0.1517(4)	4.90
C(18)	0.4089(4)	0.5741(4)	0.0391(4)	4.43
C(19)	0.4734(3)	0.3272(5)	0.1096(3)	4.00
C(21)	0.1911(3)	0.3523(3)	0.0864(3)	2.14
C(22)	0.0848(3)	0.3454(3)	0.0277(3)	2.30
C(23)	0.0471(3)	0.2966(3)	0.0790(3)	2.64
C(24)	0.1226(3)	0.2721(4)	0.1722(3)	2.71
C(25)	0.2070(3)	0.3026(3)	0.1772(3)	2.43
C(26)	0.3045(3)	0.2882(4)	0.2596(3)	3.61
C(27)	0.1063(4)	0.2146(4)	0.2478(4)	3.90
C(28)	-0.0569(3)	0.2700(4)	0.0463(4)	4.01
C(29)	0.0328(3)	0.3952(4)	-0.0690(3)	2.91
C(31)	0.2139(3)	0.0737(4)	0.0350(3)	2.65
C(32)	0.1527(3)	0.0443(3)	-0.0654(3)	2.39
C(33)	0.2021(3)	-0.0211(3)	-0.0960(3)	2.56
C(34)	0.2968(3)	-0.0393(3)	-0.0190(3)	2.84
C(35)	0.3059(3)	0.0155(4)	0.0579(3)	2.76
C(36)	0.3890(4)	0.0167(4)	0.1551(4)	4.09
C(37)	0.3725(4)	-0.1048(4)	-0.0304(4)	4.26
C(38)	0.1673(4)	-0.0717(4)	-0.1920(3)	3.96
C(39)	0.0492(3)	0.0765(4)	-0.1176(4)	3.51
C(110)	0.3579(3)	0.1926(4)	-0.0784(3)	3.31
C(210)	0.2310(3)	0.4704(4)	0.0975(3)	2.98
C(310)	0.1708(4)	0.0445(4)	0.1000(4)	3.89

1.70 (s, 12H,  $CH_3$ ); 2.52 (s, 2H, CH) ppm. MS (70 eV, EI):  $m/z$  432 ( $[M]^+$ ), 311 ( $[M - C_9H_{13}]^+$ ).

(b) To a vigorously stirred solution of 4.48 g (12.9 mmol) of **1** in 80 ml of diethyl ether were added 1.14 g (12.9 mmol) of dry  $NaC_5H_5$ . The mixture was stirred for a further 12 h; then the yellow solution was filtered through a D4 frit, concentrated to 40 ml and kept at  $-30^\circ C$  for 24 h. Colourless needles of **2** were obtained with a total yield of 2.7 g (48%).

#### 4.4. Tris(pentamethylcyclopentadienyl)gallium(III) (**3**)

In a 100 ml Schlenk flask,  $GaCl_3$  (5.01 g, 28.4 mmol) was dissolved in 80 ml of diethyl ether at  $-78^\circ C$ . The mixture was allowed to warm to room temperature and 13.49 g (85.3 mmol) of  $NaC_5Me_5$  were added with vigorous stirring. After 12 h stirring, the yellow solution was filtered through a D4 frit leaving a white precipitate, which was washed with diethyl ether ( $3 \times 20$  ml). The combined filtrate and washings were concentrated to 50 ml and kept at  $-30^\circ C$  for 24 h to yield pure **3** as colourless needles. Concentration of the remaining solution yielded a second crop. The total yield was 7.48 g (55%). Anal. Found: C, 74.86; H, 9.49.  $C_{30}H_{45}Ga$  (**3**) calcd: C, 75.79; H, 9.54%.  $^1H$  NMR ( $C_6D_6$ ,  $25^\circ C$ , 270 MHz): 1.73 (s,  $CH_3$ ) ppm.  $^{13}C$  NMR ( $C_6D_6$ ,  $25^\circ C$ , 67.89 MHz): 13.29 ( $CH_3$ ); 123 ( $C_5$ ) ppm. MS (70 eV, EI):  $m/z$  474 ( $[M]^+$ ), 339 ( $[M - C_{10}H_{15}]^+$ ).

#### 4.5. X-ray crystallographic analysis of **3**

Suitable crystals of **3** were obtained by slow crystallization of a sample of **3** from diethyl ether at  $-30^\circ C$ . The crystals were stored under solvent. A small amount of the suspension was transferred into an apparatus similar to that described by Veith and Bärninghausen [11] and a crystal of approximately 0.35 mm length was selected, glued with grease to a glass fibre and placed in the nitrogen stream of the diffractometer. The data collection was carried out with an Enraf-Nonius CAD-4 automatic diffractometer controlled by a  $\mu$ -VAX II computer and equipped with a low temperature device. The lattice parameters were obtained from the least squares refinement of the  $2\theta$  values of 25 reflections in the range  $16.2^\circ \leq 2\theta \leq 26.2^\circ$ . Reflections were scanned by the  $\omega$ - $2\theta$  scan technique. Three standard reflections were measured at 2 h intervals and showed a decay of 2.6%; the data were corrected accordingly. The intensity data were corrected for Lorentz, polarization and absorption effects and anomalous dispersion [12]. A summary of the data collection details and final lattice parameters are given in Table 3. The position of the Ga atom was determined from a Patterson synthesis [13] and the coordinates of the remaining

carbon atoms were determined by differential Fourier synthesis [14]. Neutral atom scattering factors for Ga and C were taken from the work of Cromer and Mann [15], and those for H were taken from ref. 16. Hydrogen atoms were included in calculated positions after anisotropic refinement of all non-hydrogen atoms, and further refinement [17] led to  $R = 0.046$  and  $R_w = 0.049$ . The fractional atomic coordinates and equivalent isotropic thermal parameters for **3** are given in Table 4. Tables of thermal parameters and hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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