

# Observation of a Ge–Li Bond: Donor-Base-Stabilized (Tris(trimethylsilyl)germyl)lithium<sup>†</sup>

Stefanie Freitag,<sup>‡</sup> Regine Herbst-Irmer,<sup>‡</sup> Lutz Lameyer,<sup>§</sup> and Dietmar Stalke<sup>\*,§</sup>

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany, and Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

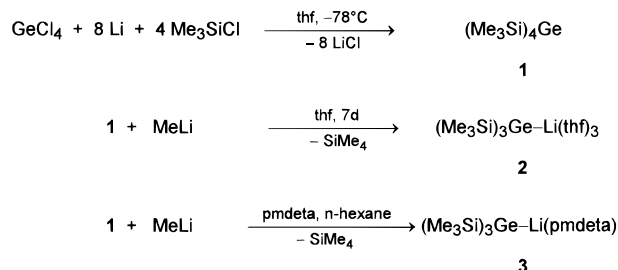
Received January 18, 1996<sup>®</sup>

**Summary:** The X-ray crystal structures of tetrakis(trimethylsilyl)germane(IV) and two donor-base-stabilized (tris(trimethylsilyl)germyl)lithium derivatives have been determined at 153 K; the latter show the first germanium–lithium bonds (2.666(6), 2.653(9) Å, respectively) characterized by X-ray structure analysis.

In comparison to the considerable effort in alkyl-lithium chemistry,<sup>1</sup> relatively little attention has been given to silyllithium chemistry.<sup>2</sup> Recently interest has been focused on the (Me<sub>3</sub>Si)<sub>3</sub>Si– ligand, because the high steric requirements along with the good solubility of the products in hydrocarbons and the electron-releasing properties make it a versatile ligand in metal–organic chemistry. However, despite such synthetic utility, up to now the chemistry of its germanium analogue, the (Me<sub>3</sub>Si)<sub>3</sub>Ge– ligand, has not been studied systematically. Structural information on lithium compounds of the heavier elements of group 14 (Ge, Sn, Pb) is even more scarce. The lack of data on germanium–lithium bonds encouraged us to study [(Me<sub>3</sub>Si)<sub>3</sub>GeLi-donor]compounds in their own right though such materials have been known for many years.<sup>3</sup> Recently, we reported the synthesis and structure of the solvent-separated ion pair [Li(12-crown-4)]<sub>2</sub>[(Me<sub>3</sub>Si)<sub>3</sub>Ge].<sup>4</sup> Here we describe the structures of (Me<sub>3</sub>Si)<sub>4</sub>Ge, **1**, [(Me<sub>3</sub>Si)<sub>3</sub>Ge–Li(thf)<sub>3</sub>] (thf = tetrahydrofuran), **2**, and [(Me<sub>3</sub>Si)<sub>3</sub>Ge–Li·pmdeta] (pmdeta = *N,N,N',N',N'*-penta-methyldiethylenetriamine), **3**. In the crystal, **2** and **3** contain a Ge–Li bond between the pyramidal (Me<sub>3</sub>Si)<sub>3</sub>Ge<sup>–</sup> anion and the (donor)<sub>n</sub>Li<sup>+</sup> cation. This is the first clear identification of a bond between germanium and an alkali metal.

Tetrakis(trimethylsilyl)germane(IV) (**1**) was synthesized according to the literature in the reaction of germanium(IV) chloride, lithium metal, and trimethyl-

## Scheme 1



chlorosilane.<sup>3</sup> The product crystallizes easily from various common organic solvents. The reaction of **1** with methyllithium in thf results in the thf-coordinated (tris(trimethylsilyl)germyl)lithium<sup>3</sup> (**2**) after stirring for 7 d (Scheme 1). Crystallization in *n*-hexane at 4 °C yields after 2 d colorless needles of **2**. The use of the donor base pmdeta leads to the formation of [(Me<sub>3</sub>Si)<sub>3</sub>Ge–Li·pmdeta], **3**. Pmdeta is added dropwise to a solution of **1** in *n*-hexane before methyllithium is added. After 5 d at –35 °C colorless crystals of **3** are obtained. The low-temperature X-ray crystal structures of both lithium compounds together with the starting material have been determined.

Different from its silicon analogue<sup>2f</sup> tetrakis(trimethylsilyl)germane(IV), **1**, adopts ideal *T<sub>d</sub>* symmetry (Figure 1) in the solid state. Due to steric strain the Me<sub>3</sub>Si groups in the spherical molecule are staggered as in a molecular gearwheel. The average Ge–Si and Si–C distances are 2.371(4) and 1.861(8) Å, respectively. The Si–Ge–Si angle is that of an ideal tetrahedral coordination (109.46(7)°).

The main feature in the monomeric structures of **2** (Figure 2) and **3** (Figure 3) is the clear occurrence of a Ge–Li bond (2.666(6) in **2** and 2.653(9) Å in **3**). These two values are almost identical with the experimentally determined average Si–Li distances of 2.653 Å in (Me<sub>3</sub>Si)<sub>3</sub>Si–Li derivatives.<sup>2d,f,g</sup> However, the comparison of the Si–Si bond length in (Me<sub>3</sub>Si)<sub>4</sub>Si (2.346(1) Å)<sup>2f</sup> and the Ge–Si bond length in (Me<sub>3</sub>Si)<sub>4</sub>Ge, **1**, of 2.371(4) Å suggests a 0.025 Å bigger radius for germanium compared to silicon. This bigger radius of germanium is reflected in a lengthened Ge–Li distance in **2** (2.666(6) Å) compared to the Si–Li bond in its silicon analogue (Me<sub>3</sub>Si)<sub>3</sub>Si–Li(thf)<sub>3</sub> (2.644(12) Å).<sup>2f</sup> Furthermore, the average Ge–Si and Si–C distances are almost unaffected by lithiation. The structural parameter which changes most by replacing a Me<sub>3</sub>Si group with the Li(donor)<sub>n</sub> group is the Si–Ge–Si angle. It is reduced from the ideal tetrahedral value of 109.46(7)° in **1** to an average value of 100.7° in **2** and **3**. The steric strain of the Li(thf)<sub>3</sub> and Li(pmdeta) groups alone clearly is not sufficient to account for that reduction, because the

<sup>†</sup> Dedicated to Prof. Dr. Erwin Weiss, Hamburg, Germany, a true protagonist of alkali metal chemistry, on the occasion of his 70th birthday.

<sup>‡</sup> Universität Göttingen.

<sup>§</sup> Universität Würzburg.

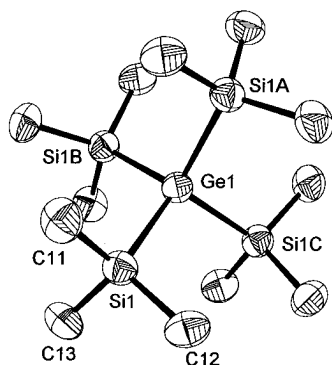
<sup>®</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1996.

(1) Recent review: Weiss, E. *Angew. Chem.* **1993**, *1056*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

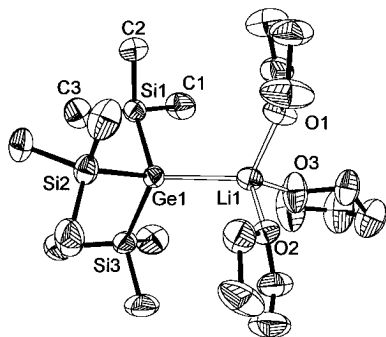
(2) (a) Schaaf, T. F.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 7593. (b) Ilsley, W. H.; Schaaf, T. F.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3769. (c) Teclé, B.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875. (d) Becker, G.; Hartmann, H.-M.; Münch, A.; Riffel, H. *Z. Anorg. Allg. Chem.* **1985**, *530*, 29. (e) Becker, G.; Hartmann, H.-M.; Hengge, E.; Schrank, F. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63. (f) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694. (g) Dias, H. V. R.; Olmstead, M. M.; Ruhlandt-Senge, K.; Power, P. P. *J. Organomet. Chem.* **1993**, *462*, 1. (h) Belzner, J.; Dehnert, U.; Stalke, D. *Angew. Chem.* **1994**, *106*, 2580; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2450.

(3) Brook, A. G.; Abdesaken, F.; Söllradl, H. *J. Organomet. Chem.* **1986**, *299*, 9.

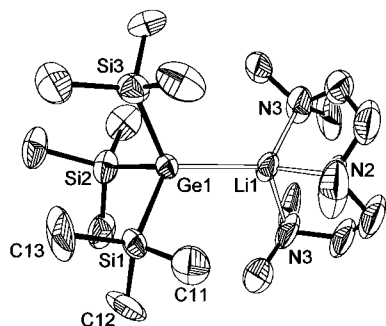
(4) Heine, A.; Stalke, D. *Angew. Chem.* **1994**, *106*, 121; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 113.



**Figure 1.** Molecular structure of **1**. The uncoordinated thf molecule present in the lattice has been omitted for clarity. For selected bond lengths and angles, see Table 1.



**Figure 2.** Molecular structure of **2**. For selected bond lengths and angles, see Table 1.



**Figure 3.** Molecular structure of **3**. For selected bond lengths and angles, see Table 1.

**Table 1. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1–3 and the Solvent-Separated (Me<sub>3</sub>Si)<sub>3</sub>Ge<sup>-</sup> Anion**

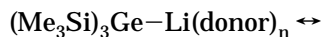
compd	Ge–Si <sup>a</sup>	Si–C	Ge–Li	Si–Ge–Si <sup>a</sup>	Si–Ge–Li <sup>a</sup>
<b>1</b>	2.371(4)	1.861(8)		109.46(7)	
<b>2</b>	2.374(1)	1.875(5)	2.666(6)	100.89(4)	117.07(14)
<b>3</b>	2.371(5)	1.912(8)	2.653(9)	100.5(2)	117.4(3)
[(Me <sub>3</sub> Si) <sub>3</sub> Ge] <sup>-b</sup>	2.368(1)	1.880(4)		101.95(3)	

<sup>a</sup> Average values of **1** including disordered Me<sub>3</sub>Si groups; given esd's are extremes. <sup>b</sup> [Li(12-crown-4)<sub>2</sub>][(Me<sub>3</sub>Si)<sub>3</sub>Ge].<sup>4</sup>

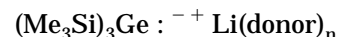
anion in the solvent-separated ion pair of [Li(12-crown-4)<sub>2</sub>][(Me<sub>3</sub>Si)<sub>3</sub>Ge]<sup>4</sup> exhibits an angle of 101.95(3)° (Table 1).

The highly polar nature of the Ge–Li bond might cause the reduction of the angles around the central germanium atom. The difference in electronegativity between germanium and lithium is about 1.0, whereas it is 0.9 between silicon and lithium.<sup>5</sup> This implies that the Ge–Li bond is even more ionic than that between

silicon and lithium. The contribution of the mesomeric extreme **b** to the explanation of the nature of the bond is even more pronounced than in the silicon–lithium bond.



**a**



**b**

The reduction of the average Si–Si–Si angle of 102.7° in (Me<sub>3</sub>Si)<sub>3</sub>Si–Li derivatives<sup>2d,f,g</sup> by another 2° in **2** and **3** indicates that the lone pair in the latter compounds is even more stereochemically active. The geometry of the Ph<sub>3</sub>Sn–Li(pmdeta)<sup>6</sup> (C–Sn–C angle 96.1(2)°) and Ph<sub>3</sub>Pb–Li(pmdeta)<sup>7</sup> (C–Pb–C angle 94.3(3)°) derivatives is even more distorted from a pure tetrahedral (sp<sup>3</sup>) arrangement. MO *ab initio* calculations<sup>7</sup> show that the Pb–Li bond is a result of s and p, rather than pure s, interaction. This trend might already be established in the Ge–Li bond.

The only other compounds containing the tris(trimethylsilyl)germyl ligand investigated by X-ray structure analysis so far are Cp\*Cl<sub>2</sub>HfGe(SiMe<sub>3</sub>)<sub>3</sub>,<sup>8</sup> (Me<sub>2</sub>N)<sub>3</sub>-TiGe(SiMe<sub>3</sub>)<sub>3</sub>,<sup>9</sup> and Cl<sub>2</sub>Sn{Ge(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>.<sup>10</sup> The main structural parameters of the ligands in these metal complexes are rather similar to those in **2** and **3**.

All three structure solutions and refinements presented here were complicated by disorder or twinning. Although highly symmetric (point group *T<sub>d</sub>*), **1** is heavily disordered. The low-temperature X-ray structure analysis of the donor-stabilized compounds **2** and **3** show that both are twinned structures which are difficult to solve and refine. **2** was refined as a racemic twin (orthorhombic space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*). **3** was refined as a twin emulating a 3-fold axis and a mirror plane in the triclinic space group *P1*. However, all crystallographical problems have been solved sufficiently to provide reliable insight into the nature of the Ge–Li bond.

## Experimental Section

All manipulations were performed under inert-gas atmosphere of dry N<sub>2</sub> with Schlenk techniques or in an argon glovebox. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained in toluene-*d*<sub>8</sub> or C<sub>6</sub>D<sub>6</sub> as solvent with SiMe<sub>4</sub> as external reference on a Bruker MSL 400, and mass spectra, on a Finnigan Mat 8230 or Varian Mat CH5 spectrometer. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

**1.** Tetrakis(trimethylsilyl)germane(IV) is prepared according to the literature<sup>3</sup> and dissolved in thf to yield colorless crystals at 4 °C.

**2.** (Tris(trimethylsilyl)germyl)lithium·3thf is as well prepared according to the literature<sup>3</sup> with the slight modification of stirring the reaction mixture at room temperature for 7 d, rather than for 14 h, to complete the reaction. A 12.35 g (33.8 mmol) amount of **1** is dissolved in 150 mL of thf and reacted

(6) Reed, D.; Stalke, D.; Wright, D. S. *Angew. Chem.* **1991**, *103*, 1539; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1459.

(7) Armstrong, D. R.; Davidson, M. G.; Moncrieff, D.; Stalke, D.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1992**, 1413.

(8) Arnold, J.; Roddick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1988**, *27*, 3510.

(9) Ovchinnikov, Y. E.; Igonin, V. A.; Timofeeva, T. V.; Lindeman, S. V.; Struchkov, Y. T.; Ustinov, M. V.; Bravo-Zhivotovskii, D. A. *Metalloorg. Khim.* **1992**, *5*, 1154.

(10) Mallela, S. P.; Geanangle, R. A. *Inorg. Chem.* **1994**, *33*, 1115.

(5) Emsley, J. *Die Elemente*; de Gruyter: Berlin, New York, 1994.

Table 2. Crystallographic Data for 1–3 at  $T = 153$  K

	1	2	3
formula	$C_{16}H_{44}OSi_4Ge$	$C_{21}H_{51}LiO_3Si_3Ge$	$C_{18}H_{50}LiN_3Si_3Ge$
fw	437.46	515.42	472.41
cryst size (mm)	$0.3 \times 0.3 \times 0.4$	$0.5 \times 0.6 \times 0.6$	$0.2 \times 0.3 \times 0.4$
space group	$P4/nmm$	$P2_12_12_1$	$P1$
$a$ (Å)	12.336(2)	10.719(2)	9.390(2)
$b$ (Å)	12.336(2)	15.773(2)	9.394(3)
$c$ (Å)	8.722(2)	18.394(3)	9.394(2)
$\alpha$ (deg)	90	90	104.96(3)
$\beta$ (deg)	90	90	104.94(3)
$\gamma$ (deg)	90	90	104.94(3)
$V$ (nm <sup>3</sup> )	1.3274(4)	3.1099(9)	0.7253(3)
$Z$	2	4	1
$\rho_c$ (Mg m <sup>-3</sup> )	1.095	1.101	1.082
$\mu$ (mm <sup>-1</sup> )	1.336	1.117	1.187
$F(000)$	472	1112	256
$2\theta$ range (deg)	8–50	8–45	9–45
no. of measd reflns	4427	6156	3964
no. of unique reflns	690	3658	3964
$R1$ ( $I > 2\sigma(I)$ )	0.045	0.029	0.036
$wR2^a$ (all data)	0.241	0.067	0.090
$g1/g2^b$	0.0937/0.0	0.0309/1.5058	0.0642/0.0831
ref params/restraints	93/135	335/487	240/556
max diff peak/hole (e nm <sup>-3</sup> )	411/–612	196/–177	357/–350

$$^a wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}. \quad ^b w^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + g2 \cdot P; \quad P = [F_o^2 + 2F_c^2] / 3.$$

with a slight excess (25 mL, 40 mmol) of methyllithium (1.6 N in ether). After removal of the solvent in vacuum, the remaining precipitate is dissolved in dry, freshly distilled *n*-hexane. Colorless needles of **2** are obtained after 2 d at 4 °C: Mp 100 °C (dec); yield 15.32 g (88%); <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta = 0.65$  (s; 27 H, SiMe<sub>3</sub>), 1.37 (m; 12H, O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 3.49 (m; 12H, O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>); <sup>7</sup>Li-NMR (155 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta = 0.58$  (s); <sup>13</sup>C-NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta = 7.29$  (s, <sup>1</sup>J<sub>Si-C</sub> = 9.8; SiMe<sub>3</sub>), 25.36 (s; O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>), 68.38 (s; O(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>); <sup>29</sup>Si-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta = -3.71$  (s, <sup>1</sup>J<sub>Si-C</sub> = 9.8); MS (EI)  $m/z$  (%) = 278 (35) GeSi<sub>3</sub>Me<sub>8</sub>, 219 (16) GeSi<sub>2</sub>Me<sub>6</sub>, 147 (25) GeSiMe<sub>3</sub>, 73 (100) SiMe<sub>3</sub>.

**(Tris(trimethylsilyl)germyl)lithium-pmdeta (3).** A 2.00 g (3.9 mmol) amount of **2** is dissolved in 40 mL of dry, freshly distilled *n*-hexane, and 1 mL (4.8 mmol) of sodium-dried pmdeta is added. The colorless precipitate can be redissolved in *n*-hexane, and after 5 d at –35 °C colorless crystals are obtained. In analogy to **2**, **3** can be prepared from **1** in *n*-hexane and pmdeta by adding methyllithium: Mp 260 °C (dec); yield 1.54 g (83%); <sup>1</sup>H-NMR (400 MHz, C<sub>7</sub>D<sub>8</sub>)  $\delta = 0.56$  (s; 27H, SiMe<sub>3</sub>), 2.05–2.15 (m; 23H, pmdeta); <sup>7</sup>Li-NMR (97 MHz, C<sub>7</sub>D<sub>8</sub>)  $\delta = 0.92$  (s); <sup>13</sup>C-NMR (100 MHz, C<sub>7</sub>D<sub>8</sub>)  $\delta = 7.48$  (s; SiMe<sub>3</sub>), 46.16 (s; N–CH<sub>3</sub>), 53.45 (s; CH<sub>2</sub>), 57.28 (s; CH<sub>2</sub>); MS (EI)  $m/z$  (%) = 278 (17) GeSi<sub>3</sub>Me<sub>8</sub>, 220 (20) GeSi<sub>2</sub>Me<sub>6</sub>, 147 (49) GeSiMe<sub>3</sub>, 73 (100) SiMe<sub>3</sub>.

**X-ray Measurements of 1–3.** The data sets were collected on a Siemens-Stoe AED using Mo K $\alpha$  radiation ( $\lambda = 0.710$  73 Å) at a temperature of 153 K.<sup>11</sup> Semiempirical absorption corrections were applied for **1** and **2**. The structures were solved by direct methods.<sup>12</sup> All non-hydrogen atoms were refined anisotropically (except disordered solvent molecules), and a riding model was employed in the refinement of the hydrogen atom positions. The structures were refined against  $F^2$  with a weighting scheme  $w^{-1} = \sigma^2 F_o^2 + (g1 \cdot P)^2 + g2 \cdot P$  where  $P = (F_o^2 + 2F_c^2) / 3$ .<sup>13</sup> **1** crystallizes with one disordered thf molecule in the asymmetric unit which was refined as a five-membered CH<sub>2</sub> ring with distances restrained to be equal. The

disordered SiMe<sub>3</sub> groups on a mirror plane were refined to a split occupancy of 0.13/0.37 with distance and rigid bond restraints. The anisotropic displacement parameters were restrained to be similar. **2** crystallizes as a racemic twin.<sup>14</sup> The fractional contribution of a second twin domain refined to 0.389(12). The thf molecules are disordered and were refined with distance and rigid bond restraints. The anisotropic displacement parameters were restrained to be similar. The structure solution and refinement of **3** was difficult since the metric symmetry of the cell emulates rhombohedral symmetry. Although the program XPREP<sup>15</sup> suggested the rhombohedral space group  $R\bar{3}m$  for the refinement, the pmdeta fragment neither fulfills the requirements of the mirror plane nor of the 3-fold axis. However, there are various strategies to refine **3**: either with a disordered pmdeta molecule in space group  $R\bar{3}m$  or with an ordered pmdeta fragment in space group  $P1$ , emulating the mirror plane and 3-fold axis as twin operations. We decided for the latter with twinning factors refined to 0.162(3), 0.168(3), 0.160(3), 0.175(3), and 0.161(3). Refinement of an inversion twin parameter<sup>16</sup> [ $x = -0.043$ (14), where  $x = 0$  for the correct absolute structure and +1 for the inverted structure] confirmed the absolute structure of **3**. Selected bond lengths and angles of **1–3** can be found in Table 1, and relevant crystallographic data, in Table 2.

**Acknowledgment.** All the authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

**Supporting Information Available:** Tables of crystal data, complete fractional coordinates and  $U$  values, and bond lengths and angles, fully labeled figures of 50% anisotropic displacement parameters, and tables of anisotropic displacement parameters for the structures **1–3** (17 pages). Ordering information is given on any current masthead page.

OM9600295

(11) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.

(12) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(13) Sheldrick, G. M. SHELXL-93, program for crystal structure refinement, Göttingen, Germany, 1993.

(14) Pratt, C. S.; Coyle, B. A.; Ibers, J. A. *J. Chem. Soc. A* **1971**, 2146.

(15) Sheldrick, G. M. SHELXTL-Plus, Release 5.01, Siemens Analytical X-ray Instruments Inc., Madison, WI.

(16) (a) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876. (b) Bernadinelli, G.; Flack, H. D. *Acta Crystallogr., Sect. A* **1985**, *41*, 500.