Methyl Substitution of Aluminum−Hydride Bonds in a Carbaalane and an Aluminum Imide

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Keywords: Aluminum / Cluster Compounds / Hydrides

The methylated compounds [(AlMe)$_6$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$] (**4**), [(AlMe)$_6$(AlNMe$_3$)$_2$(CCH$_2$CH$_2$SiMe$_3$)$_6$] (**5**) and [(AlMe)$_6$(NCH$_2$C$_4$H$_3$S)$_6$] (**6**) were synthesized in good yields from the corresponding hydride derivatives by treatment with AlMe$_3$ in toluene. The X-ray single crystal structures of **4**·xC$_7$H$_8$, **4**·4C$_7$H$_8$ and **6** were determined. In **4**·xC$_7$H$_8$ the solvent molecules are arranged in infinite channels along the *c* axis.

The chemistry of carbaalanes and aluminum imide (or iminoalane) cage compounds is growing rapidly. After the synthesis of the cluster cores their derivatisation is an attractive goal for synthetic chemists. The aluminum−hydride bonds in the hydroalumination products can be converted into other functionalities. Recently, we have used various reagents to substitute the hydrides in the carbaalane [(AlH)$_6$(AlNMe$_3$)$_2$(CCH$_2$R)$_6$] (R = Ph **1**, CH$_2$SiMe$_3$ **2**) and in the aluminum imide [(AlH)$_6$(NCH$_2$C$_4$H$_3$S)$_6$] (**3**) to yield halogen and alkynyl derivatives.[1−6] Herein we report further attempts to substitute the hydrides by methyl groups.

Initial investigations were carried out with protic reagents such as alcohols and secondary amines. The reaction of **1** with six equivalents of isopropanol results in the formation of impure compounds and decomposition of the cluster. The reaction of **1** with six equivalents of R$_2$NH (R = Et, SiMe$_3$) in toluene gave no gas evolution either at room temperature or upon heating the mixture to its boiling point; crystals of **1** were recovered from the reaction mixture. Similar reactions were undertaken with **3**. Again, reactions with alcohols led to decomposition of the cage and amines did not properly react with the hydrides. A partial substitution of **1**, however, was achieved with a protic reagent: ethynylferrocene reacted at elevated temperatures leading to the formation of terminal alkynyl-substituted products.[3]

Bis(trimethylsilyl) ether [(Me$_3$Si)$_2$O] reacts with neat *i*Bu$_2$AlH under reflux conditions to form (Me$_3$SiOAl*i*Bu$_2$)$_2$, while AlH$_3$·NMe$_3$ does not react under these conditions.[7] However, we found no reaction or significant solubility of **1** in neat boiling (Me$_3$Si)$_2$O (b.p. 101 °C). AlH$_3$·NMe$_3$ forms the soluble aluminum sulfide compounds [(Me$_3$NAl)$_4$S$_6$] and [(Me$_3$NAl)$_2$(Me$_3$NAlH)$_2$S$_5$] upon reaction with (Me$_3$Si)$_2$S in hot toluene.[8] Treatment of **1** with an excess (ca. 18 equiv.) of (Me$_3$Si)$_2$S in boiling toluene for one day, and subsequent workup, afforded crystals of the starting material in moderate yield. Moreover, (Me$_3$Si)$_2$ did not react with **1** under similar conditions and crystals of **1** were again recovered. No reaction of (Me$_3$Si)$_2$ with *i*Bu$_2$AlH has been reported.[9]

When a suspension of **1** in toluene is treated with an excess of AlMe$_3$ at room temperature the solubility improves, and after several hours of stirring the precipitate that forms is converted into fine, colorless, needle- or rod-shaped crystals. Filtering off these crystals and storing the solution at 4 °C afforded additional crystals of the same shape. The X-ray single crystal structure analysis showed these to be the expected compound [(AlMe)$_6$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$] (**4**) with toluene. Crystals of [(AlMe)$_6$(AlNMe$_3$)$_2$(CCH$_2$Ph)$_6$]·4C$_7$H$_8$ (**4**) 4C$_7$H$_8$) were obtained at −25 °C from the supernatant solution. The reaction of **2** with AlMe$_3$ for four hours afforded [(AlMe)$_6$(AlNMe$_3$)$_2$(CCH$_2$CH$_2$SiMe$_3$)$_6$] (**5**) in good purity after removal of all volatiles at 50 °C in vacuo (Scheme 1).

In the same manner, the hexameric aluminum imide [(AlH)$_6$(NCH$_2$C$_4$H$_3$S)$_6$] **3** was treated with AlMe$_3$ in toluene at room temperature to yield the methylated species [(AlMe)$_6$(NCH$_2$C$_4$H$_3$S)$_6$] (**6**). The reaction of **3** with diethylzinc in THF/toluene at room temperature gave [(AlEt)$_6$(NCH$_2$C$_4$H$_3$S)$_6$] (**7**), where the hydrides have been substituted by ethyl groups; no coordination of diethylzinc to the thiophenyl groups was found. The substitution of the hydridic hydrogens of hexameric aluminum imides, prepared from aluminum hydrides and primary amines, was first reported in the 1970s. Partially and fully alkylated

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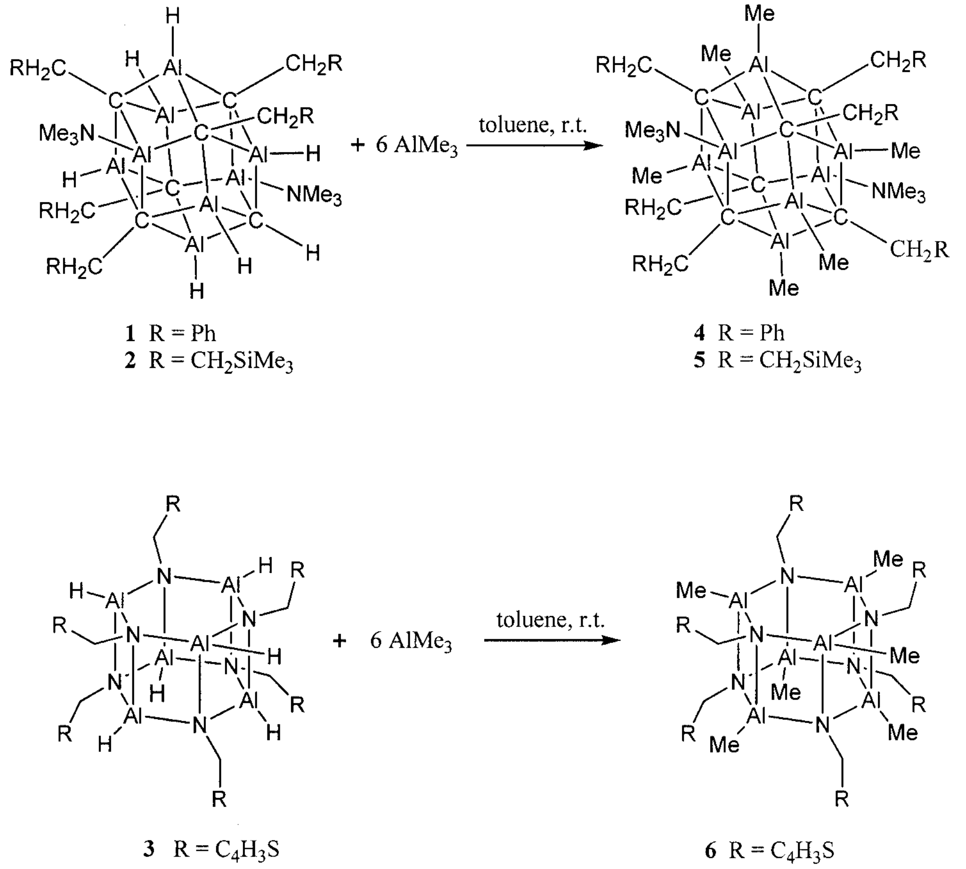
DOI: 10.1002/ejic.200400347



1 R = Ph
2 R = CH_2SiMe_3

4 R = Ph
5 R = CH_2SiMe_3

3 R = C_4H_3S

6 R = C_4H_3S

Scheme 1

species were isolated from reactions with AlR_3 (R = Me, Et) giving rise to **6** and **7**, which were not structurally characterized.[10] Only substitution and no degradation of the cage or cluster structures is observed upon treatment with AlR_3 (R = Me, Et) in these reactions. Methyl-substituted aluminum imides prepared from primary amines and $AlMe_3$ at elevated temperatures often show different degrees of oligomerization depending on the size of the organic groups.[11] A prominent example is the planar alumazene.[12]

The first crystals of compound **4** with toluene crystallize in the trigonal space group $R\bar{3}$. The solvent molecules (toluene) are disordered and are located in channels along the *c* axis that are only partially occupied and could not be successfully refined. The packing of **4** is shown in Figure 1. The width of the channels is about 12.2 Å (calculated from the centers of the atoms), which is approximately the size of **4**. A similar packing was found in the crystal structure of an iron compound with seven hexane molecules within the channel.[13] Compound $\mathbf{4}{\cdot}4C_7H_8$ crystallizes at −25 °C in the monoclinic space group *C*2/*c* with one half of a molecule and two molecules of toluene in the asymmetric unit (Figure 2 and Table 1). Compound **6** crystallizes in the triclinic space group $P\bar{1}$ with half a molecule in the asymmetric unit (Figure 3 and Table 2). One thiophenyl group is distorted and two positions of the thiophene ring were refined for S(1). The basic structure of the new compounds is nearly identical to their starting materials. The Al−C bond lengths for the methyl groups range from 1.973(2) Å to 1.976(2) Å in $\mathbf{4}{\cdot}4C_7H_8$ and 1.937(4) Å to 1.978(5) Å in **6**. For comparison, the Al−C bond lengths in the cluster **4** are longer [from 2.036(2) Å to 2.118(2) Å] than the single bonds of the methyl groups to aluminum.

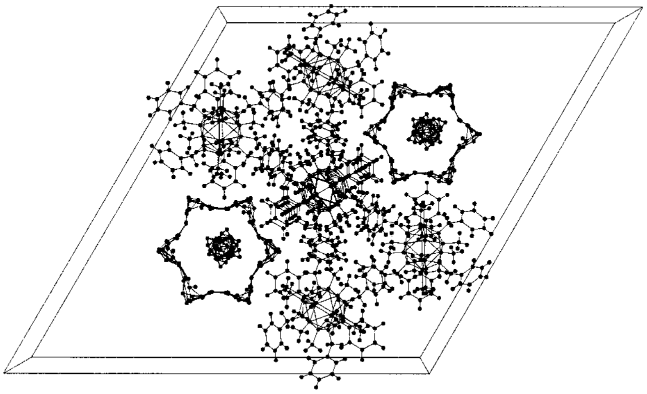


Figure 1. Packing diagram of $\mathbf{4}{\cdot}xC_7H_8$; perspective view along the *c* axis; the disordered solvent molecules are pictured as simple dots; the centers of the channels are located on the C_3 axes

Compound **4** is only poorly soluble and no NMR spectra of sufficient quality could be recorded. The EI mass spectrum only shows C−H fragments. The methyl groups of **5** appear as a singlet in the ^1H NMR spectrum (δ = 0.2 ppm).

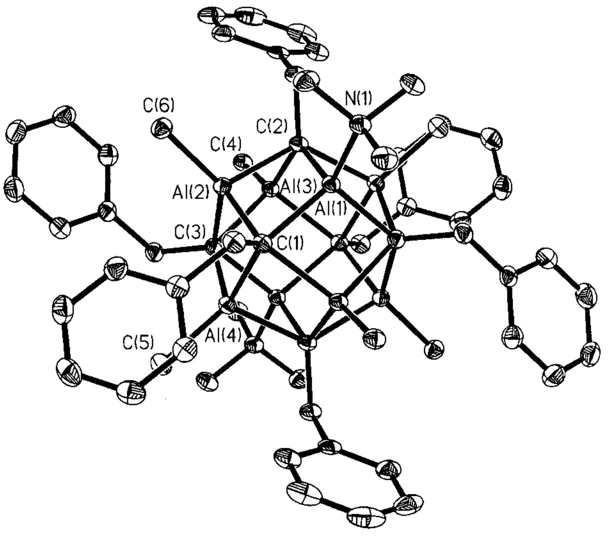


Figure 2. Molecular structure of **4**·$4C_7H_8$; hydrogen atoms and solvent molecules are omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for **4**·$4C_7H_8$

Al(1)−N(1)	2.008(1)	Al(2)−C(6)	1.973(2)
Al(1)−C(2)	2.036(2)	Al(2)−C(2)	2.117(2)
Al(1)−Al(32)	2.585(1)	Al(3)−Al(2)	2.667(1)
C(6)−Al(2)−C(3)	129.4(1)	C(6)−Al(2)−C(1)	113.5(1)
C(6)−Al(2)−C(2)	112.4(1)	C(4)−Al(3)−C(2)	130.8(1)
C(4)−Al(3)−C(3)	112.4(1)	C(4)−Al(3)−C(3)	112.0(1)

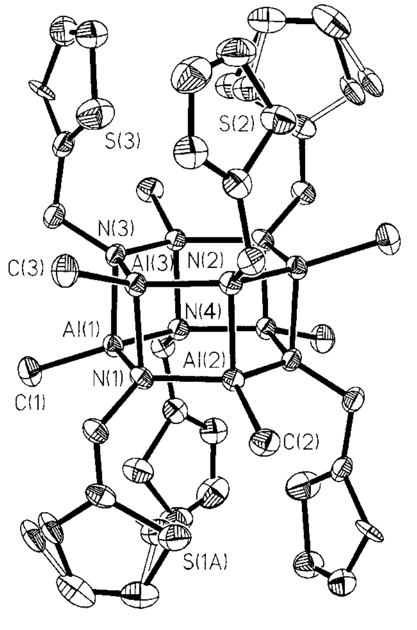


Figure 3. Molecular structure of **6**; hydrogen atoms are omitted for clarity

Table 2. Selected bond lengths (Å) and angles (°) for **6**

Al(1)−N(1)	1.886(4)	Al(1)−N(3)	1.986(3)
Al(1)−C(1)	1.978(5)	Al(2)−N(1)	1.877(3)
Al(2)−N(2)	1.982(3)	Al(2)−C(2)	1.937(4)
Al(3)−N(3)	1.879(3)	Al(3)−N(1)	1.986(3)
Al(3)−C(3)	1.94(1)		
N(4)−Al(1)−N(1)	113.8(2)	N(1)−Al(1)−N(3)	91.3(2)
N(1)−Al(1)−C(1)	119.3(2)	N(1)−Al(1)−C(1)	119.6(2)

The cluster carbon atoms resonate at $\delta = 20.3$ ppm in the ^{13}C NMR spectrum and a broad singlet ($\delta = 155.4$ ppm) is observed in the ^{27}Al NMR spectrum of **5**. In general, the NMR resonances of **5** are shifted downfield compared to the starting material **2** and its halogen derivatives, except for the cluster carbon atoms in the ^{13}C NMR spectrum. The EI mass spectrum provides a molecular ion peak at $m/z = 1102.6$ for **5**. The singlet resonance for the protons of the methyl groups in the ^{1}H NMR spectrum of **6** is at $\delta = -0.52$ ppm and is not shifted as far downfield as that for **5**. The NMR resonances are in agreement with the observed composition. The EI mass spectrum provides no molecular ion peak for **6**, although an ion corresponding to $[M^+ - CH_4]$ was observed at $m/z = 903$.

In conclusion, the cluster cores of both the carbaalane and aluminum imide containing reactive Al−H bonds can be effectively replaced by methyl groups upon reaction with $AlMe_3$.

Experimental Section

General Remarks: All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) using Schlenk-line and glove-box techniques. The samples for spectral measurements were prepared in a dry box. Solvents were purified according to conventional procedures and were freshly distilled prior to use. NMR spectra were recorded on a Bruker AM 200 instrument, and the chemical shifts are reported with reference to TMS. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS−SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

Synthesis of $[(AlMe)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (4): $AlMe_3$ (1.90 mL of a 2.0 M solution in toluene, 3.80 mmol, 20 equiv.) was added to a fine suspension of **1** (0.18 g, 0.188 mmol, 1.0 equiv.) in toluene (20 mL). The mixture was stirred for 15 h during which time the solid turned into fine crystals. After filtration, additional needle- or rod-shaped crystals with of **4**·xC_7H_8 were obtained at 4 °C. Storing the supernatant solution at −25 °C gave crystals of **4**·$4C_7H_8$. The crystals were dried in vacuo. Yield 0.17 g (0.16 mmol, 87%). M.p.: ca. 240 °C (decomposition). IR (Nujol, KBr plates): $\tilde{\nu}$ = 1653, 1262, 1100, 971, 810, 750, 574 cm^{-1}. $C_{60}H_{78}Al_8N_2$ (1043.13): calcd. C 69.08, H 7.54, N 2.69; found 67.83, H 7.58, N 2.85.

Synthesis of $[(AlMe)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (5): $AlMe_3$ (1.00 mL of a 2.0 M solution in toluene, 2.00 mmol, 15.6 equiv.) was added to a solution of **2** (0.13 g, 0.128 mmol, 1.0 equiv.) in toluene (5 mL). The solution was stirred for 4 h, all volatiles were removed in vacuo and the crude product was dried at 50 °C in vacuo giving **5** in a quantitative yield possibly admixed with a little Me_2AlH. M.p.: 210 °C (color change), 246 °C (full decomposition). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 0.10$ [s, 54 H, $Si(CH_3)_3$], 0.2 (br. s, 18 H, $AlCH_3$), 1.00 (ddd, J = 9.0, 4.1, 4.1 Hz, 12 H, Me_3SiCH_2), 2.16 (ddd, J = 9.0, 4.1, 4.1 Hz, 12 H, CCH_2), 2.17 [s, 18 H, $N(CH_3)_3$] ppm. ^{13}C NMR (126 MHz, C_6D_6): $\delta = -4.1$ (broad, $AlCH_3$), −1.63 [$Si(CH_3)_3$], 20.3 (cluster-*C*), 25.9 (Me_3SiCH_2), 27.9

(CH_2C), 46.9 [$N(CH_3)_3$] ppm. ^{27}Al NMR (78.2 MHz, C_6D_6): δ = 155.4 (s, very broad) ppm. ^{29}Si NMR (99.4 MHz, CD): $\delta = -0.82$ ppm. MS (EI): *m*/*z* (%) = 1102.6 (3) [M^+], 1043.5 (48) [M^+ − NMe], 998.5 (71) [M^+ − NMe − NHMe], 984.5 (100) [M^+ − 2NMe]. IR (Nujol, KBr plates): $\tilde{\nu}$ = 1318, 1258, 1182, 1022, 862, 828, 763, 723, 672, 593, 485 cm^{-1}. $C_{48}H_{114}Al_8N_2Si_6$ (1103.80): calcd. C 52.23, H 10.41, N 2.54; found C 51.98, H 10.34, N 2.61.

Synthesis of [$(AlMe)_6(NCH_2C_4H_3S)_6$] (6): $AlMe_3$ (2.7 mL of a 2.0 M solution in heptane, 5.40 mmol, 9.0 equiv.) was added dropwise to a solution of **3** (0.50 g, 0.60 mmol, 1.0 equiv.) in toluene (20 mL). The resultant mixture was stirred overnight at room temperature and filtered. The filtrate was reduced to 20 mL in vacuo and stored at 0 °C for several days to obtain colorless crystals of **6** (0.40 g, 0.435 mmol, 73%). M.p.: 246 °C (decomposition). ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -0.52$ (s, 18 H, $AlCH_3$), 4.28 (s, 12 H, NCH_2), 6.70, 6.80, 7.20 (m, 18 H, C_4H_3S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -7.2$ (Al−CH_3), 43.5 (NCH_2), 123.7, 124.9, 127.5, 148.3 (C_4H_3S) ppm. IR (nujol, NaCl plates): $\tilde{\nu}$= 1340 (m), 1254 (m), 1210 (s), 1167 (w), 1059 (w), 1014 (s), 980 (s), 965 (s), 943 (s), 848 (s), 747 (s), 734 (s), 683 (s) cm^{-1}. EI-MS: *m*/*z* (%) = 903 (100) [M^+ − CH_4], 835 (8) [$C_{30}H_{36}Al_6N_6S_6^+$], 113 (52) [$CH_2C_4H_3SNH_2^+$], 97 (72) [$CH_2C_4H_3S^+$]. $C_{36}H_{48}Al_6N_6S_6$ (919.04): calcd. C 47.05, H 5.26, N 9.14; found C 46.53, H 4.89, N 8.96.

X-ray Structure Determination of 4·4C_7H_8, 4·*x*C_7H_8 and 6: A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **4**·4C_7H_8 were collected on SMART instrument, and for **4**·*x*C_7H_8 and **6** the data were collected on a STOE IPDS2 diffractometer. The structures were solved by direct methods and refined with full-matrix least-squares on F^2 using SHELX-97.[14,15] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from the International Tables for X-ray Crystallography.[16] Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The restraints in **4**·4C_7H_8 are due to the distortions of the toluene molecules and in **6** the quality of the data is not as good as expected due to the breakdown of the low-temperature equipment and disorder in one of the thiophenyl groups. The crystallographic data is summarized in Table 3.

CCDC-237048 (for **4**·*x*C_7H_8), -237049 (for **4**·4C_7H_8) and -237050 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften is gratefully acknowledged.

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Table 3. Crystal data and refinement details. Compound **4**·xC_7H_8 was refined without the solvent molecules

Compound	**4**·*x*C_7H_8	**4**·4C_7H_8	**6**
Empirical formula	$C_{60}H_{78}Al_8N_2$	$C_{88}H_{110}Al_8N_2$	$C_{36}H_{48}Al_6N_6S_6$
Molecular mass	1043.08	1411.62	919.04
T	133(2) K	100(2) K	133(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å
Crystal system	trigonal	monoclinic	triclinic
Space group	$R\bar{3}$	$C2/c$	$P\bar{1}$
Unit cell dimensions	a = 40.445(6) Å	a = 25.468(5) Å	a = 10.347(9) Å
	b = 40.445(6) Å	b = 15.899(3) Å	b = 10.284(9) Å
	c = 11.670(2) Å	c = 23.256(5) Å	c = 10.955(9) Å
	α = 90°	α = 90°	α = 99.537(7)°
	β = 90°	β = 122.69(3)°	β = 100.632(7)°
	γ = 120°	γ = 90°	γ = 101.027(7)°
V	16530(10) Å^3	7925(3) Å^3	1099.99(16) Å^3
Z	9	4	1
D_{calcd}	0.943 Mg/m^3	1.183 Mg/m^3	1.387 Mg/m^3
μ	0.142 mm^{-1}	1.317 mm^{-1}	0.466 mm^{-1}
F(000)	5004	3024	480
Crystal size	0.30 × 0.20 × 0.10 mm^3	0.10 × 0.10 × 0.05 mm^3	0.20 × 0.20 × 0.10 mm^3
θ	1.74 to 24.76°	3.46 to 59.06°	1.93 to 25.08°
Index range	$-47 \le h \le 47$	$-27 \le h \le 28$	$-12 \le h \le 11$
	$-47 \le k \le 45$	$-17 \le k \le 17$	$-11 \le k \le 12$
	$-13 \le l \le 13$	$-25 \le l \le 25$	$-12 \le l \le 12$
Reflexes collected/unique	57395/6280	17157/5549	6421/3579
Completeness to θ	99.7%	96.9%	91.5%
R_{int}	0.2439	0.0246	0.0431
Data/restraints/parameters	6280/0/357	5549/92/484	3579/0/254
Goodness-of-fit on F^2	1.035	1.051	1.046
R values [$I > 2\sigma(I)$]	$R_1 = 0.0873$, $wR_2 = 0.1747$	$R_1 = 0.0281$, $wR_2 = 0.0746$	$R_1 = 0.0589$, $wR_2 = 0.1574$
R values (all data)	$R_1 = 0.1501$, $wR_2 = 0.2267$	$R_1 = 0.0310$, $wR_2 = 0.0766$	$R_1 = 0.0745$, $wR_2 = 0.1693$
Largest diff. peak and hole (max and min)	0.704 and −0.485 e·Å^{-3}	0.232 and −0.190 e·Å^{-3}	0.883 and −0.738 e·Å^{-3}

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Received April 29, 2004