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Synthesis and structures of the chelating diamido zirconium and hafnium compounds

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The chelating diamide lithium complex [$Me_2Si\{NLiCH(Me)Ph\}_2]_2$ (1) was synthesized. The X-ray structure of complex 1 reveals that in the solid state it is a dimer; every lithium atom is three coordinated. The [$\{Me_2Si\{NCH(CH_3)Ph\}_2\}ZrCl_2LiCl(OEt_2)_2]_2$ (2) and [$\{Me_2Si\{NCH(CH_3)Ph\}_2\}HfCl_2LiCl(OEt_2)_2]_2$ (3) complexes were formed by treatment of complex 1 with $ZrCl_4$ and $HfCl_4$ respectively in diethyl ether at ambient temperature. Complexes (2) and (3) were also characterized by X-ray single-crystal diffraction. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: chelating; diamide; zirconium; hafnium

INTRODUCTION

To develop new-generation alkene polymerization catalysts in which the cyclopentadienyl groups are replaced by other ligands has been one of the most noteworthy research fields in the past few years.[1–3] A recent review on olefin polymerization catalysts identified various types of spectator ligand, other than those of cyclopentadienyl type, many of which are nitrogen centred, such as porphyrins,[4] tetraazaannulenes,[5] tetradentate Schiff-base ligands,[6] (hydroxyphenyl) oxazolines,[7] benzamidinates,[8–13] pyrollyls,[14] and amido- and alkoxy-pyridines.[15–18] But chelating diamide Group 4 catalysts have been studied very rarely, despite the straightforward synthesis of Group 4 diamide complexes and the wide potential for ligand variation.[19,20] Here, we report a chelating diamide ligand having a chiral carbon atom and its lithium, zirconium and hafnium complexes.

RESULTS AND DISCUSSION

Preparations

The reaction of 1-phenylethylamine with dichlorodimethylsilane and then with *n*-butyllithium affords dilithium amide [$Me_2Si\{NLiCH(CH_3)Ph\}_2]_2$ (**1**) in 90% yield, as shown in Scheme 1. Treatment of **1** with $ZiCl_4$ or $HfCl_4$ in diethyl ether gives the chelating diamido zirconium (**2**) or hafnium (**3**) complex respectively in good yield (80% and 90% respectively). All products (**1**–**3**) are colourless crystals and air sensitive. Complexes **1**–**3** were characterized by multinuclear magnetic resonance (^1H, ^{13}C and ^7Li), elemental analyses and X-ray diffraction determination.

Crystal structure

Colourless cubic crystals of compound **1** were crystallized from Et_2O at −15 °C. Figure 1 shows the molecular structure of the lithium compound [$Me_2Si\{NLiCH(CH_3)Ph\}_2]_2$ (**1**) and gives the atom numbering scheme. Selected bond lengths and angles of the compound are listed in Table 1. Compound **1** is a dimer in the solid state. Four lithium atoms and four nitrogen atoms form a tetragonal prism. Each lithium atom is coordinated by three nitrogen atoms. Two carbon atoms in the phenyl ring coordinate weakly with the adjacent lithium atom. Colourless block crystals of compounds **2** and **3** were crystallized from Et_2O. Both compounds **2** and **3** are dimeric, bridged by two chlorine atoms in the solid state. M(1)–Cl(1)–M(1A)–Cl(1A) (M = Zr or Hf) forms a quadrangle. The molecular structures and the atom numbering schemes of compounds **2** and **3** are shown in Figs 2 and 3 respectively. Selected bond lengths and angles of compounds **2** and **3** are listed in Tables 2 and 3 respectively. Selected geometrical parameters of compounds **1, 2** and **3** are listed in Table 4.

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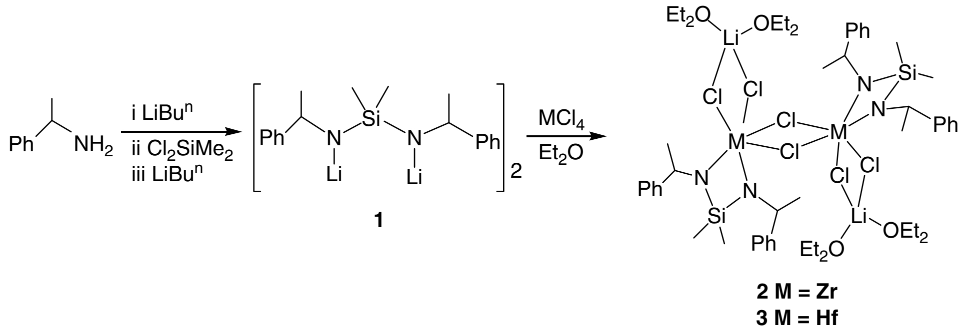

Scheme 1. Synthesis of compounds **1, 2** and **3**.

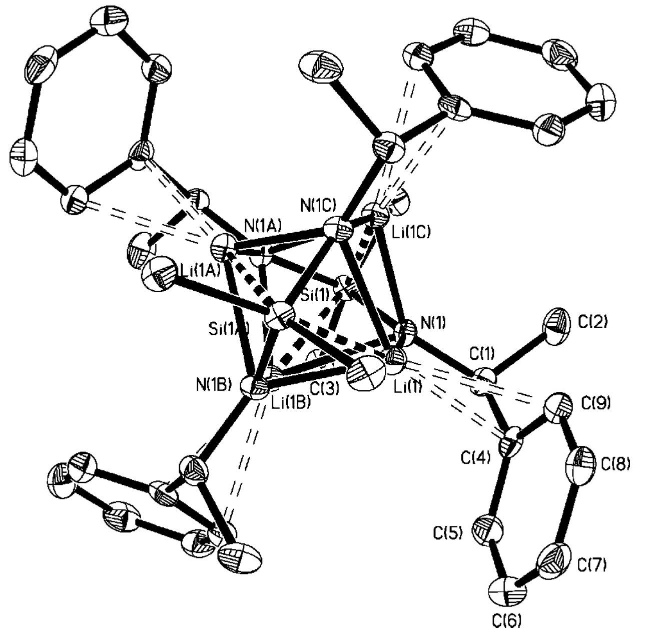

Figure 1. Molecular structure of compound **1**.

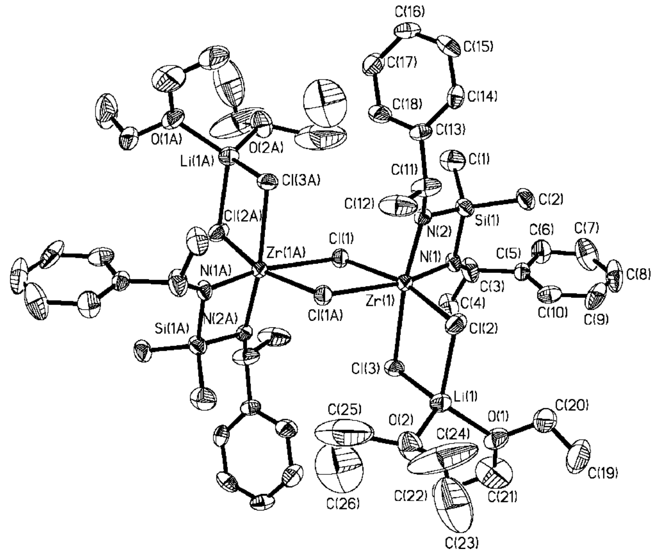

Figure 2. Molecular structure of compound **2**.

Table 1. Selected bond lengths and angles of compound **1**[a]

Bond lengths (Å)		Bond angles (°)	
Li(1)–N(1)	2.057(5)	N(1)–Li(1)–N(1B)	113.1(2)
Li(1)–N(1B)	2.074(5)	N(1)–Li(1)–N(1C)	107.1(2)
Li(1)–N(1C)	2.224(5)	N(1B)–Li(1)–N(1C)	73.13(18)
Li(1)–Si(1A)	2.522(5)	N(1)–Li(1)–Si(1A)	138.2(2)
		N(1B)–Li(1)–Si(1A)	42.70(11)
		N(1C)–Li(1)–Si(1A)	42.03(10)

[a] Symmetry transformations used to generate equivalent atoms: #1, $y, -x+1, -z+2$; #2, $-y+1, x, -z+2$; #3, $-x+1, -y+1, z$.

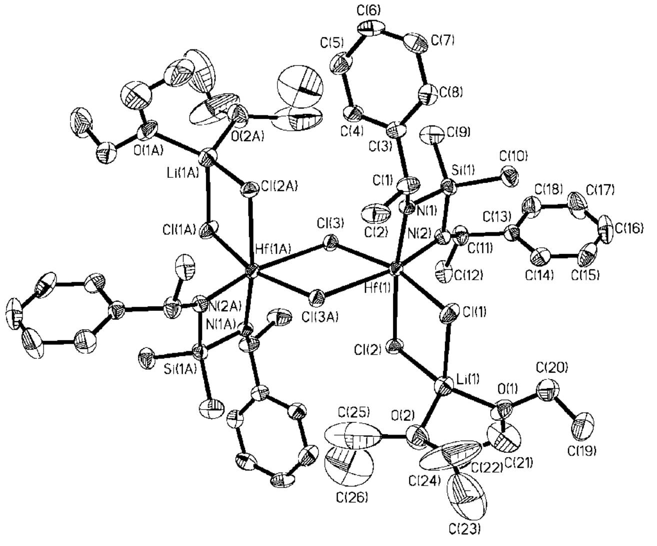

Figure 3. Molecular structure of compound **3**.

EXPERIMENTAL

Instruments

All experiments were performed under nitrogen or argon using standard Schlenk techniques. NMR spectra were

Table 2. Selected bond lengths and angles of compound **2**[a]

Bond lengths (Å)		Bond angles (°)	
Zr(1)–N(1)	1.995(4)	N(1)–Zr(1)–N(2)	78.17(14)
Zr(1)–N(2)	2.015(4)	N(1)–Zr(1)–Cl(2)	101.78(13)
Zr(1)–Cl(2)	2.5334(17)	N(2)–Zr(1)–Cl(2)	89.81(12)
Zr(1)–Cl(3)	2.5696(14)	N(1)–Zr(1)–Cl(3)	98.98(11)
Zr(1)–Cl(1)	2.5991(16)	N(2)–Zr(1)–Cl(3)	171.22(12)
Zr(1)–Cl(1A)	2.6809(14)	Cl(2)–Zr(1)–Cl(3)	82.62(5)
O(1)–Li(1)	1.931(10)	N(1)–Zr(1)–Cl(1)	91.34(13)
O(2)–Li(1)	1.912(10)	N(2)–Zr(1)–Cl(1)	99.60(12)
Li(1)–Cl(3)	2.347(10)	Cl(2)–Zr(1)–Cl(1)	165.23(5)
Li(1)–Cl(2)	2.358(9)	Cl(3)–Zr(1)–Cl(1)	88.72(5)
		N(1)–Zr(1)–Cl(1A)	166.84(13)
		N(2)–Zr(1)–Cl(1A)	97.20(10)
		Cl(2)–Zr(1)–Cl(1A)	90.44(5)
		Cl(3)–Zr(1)–Cl(1A)	87.33(4)
		Cl(1)–Zr(1)–Cl(1A)	77.18(5)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x+1, -y+2, -z+1$.

Table 3. Selected bond lengths and angles of compound **3**[a]

Bond lengths (Å)		Bond angles (°)	
Hf(1)–N(2)	1.998(4)	N(2)–Hf(1)–N(1)	78.47(14)
Hf(1)–N(1)	2.013(3)	N(2)–Hf(1)–Cl(1)	102.41(11)
Hf(1)–Cl(1)	2.5073(13)	N(1)–Hf(1)–Cl(1)	89.65(10)
Hf(1)–Cl(2)	2.5477(12)	N(2)–Hf(1)–Cl(2)	99.13(10)
Hf(1)–Cl(3)	2.5642(12)	N(1)–Hf(1)–Cl(2)	171.54(10)
Hf(1)–Cl(3A)	2.6647(13)	Cl(1)–Hf(1)–Cl(2)	82.91(4)
Li(1)–O(2)	1.904(10)	N(2)–Hf(1)–Cl(3)	91.25(11)
Li(1)–O(1)	1.909(9)	N(1)–Hf(1)–Cl(3)	99.51(10)
Li(1)–Cl(2)	2.367(9)	Cl(1)–Hf(1)–Cl(3)	164.89(4)
Li(1)–Cl(1)	2.375(9)	Cl(2)–Hf(1)–Cl(3)	88.62(4)
		N(2)–Hf(1)–Cl(3A)	166.94(11)
		N(1)–Hf(1)–Cl(3A)	97.71(11)
		Cl(1)–Hf(1)–Cl(3A)	89.97(4)
		Cl(2)–Hf(1)–Cl(3A)	86.36(4)
		Cl(3)–Hf(1)–Cl(3A)	76.97(4)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$.

recorded on a Bruker DRX300 instrument at 300.13 MHz (^{1}H), 75.47 MHz (^{13}C) and 116.64 MHz (^{7}Li); chemical shift values δ are given in parts per million relative to $SiMe_4$ and aqueous LiCl. Elemental analyses were performed on a Vario-III analyser.

Synthesis

Solvents were purified by distillation from an appropriate drying agent (diethyl ether from sodium–benzophenone, hexane from sodium–potassium alloy). All the other reagents were purchased from ACROS.

Synthesis of the title compounds

$Me_2Si[NHCH(CH_3)Ph]_2$

To a stirred solution of $PhCH(CH_3)NH_2$ (15.3 g, 126 mmol) in hexane (300 ml) was added dropwise Li^{n}Bu (126 mmol) solution in hexane at 0 °C. The mixture was then warmed to room temperature and stirred for 12 h. Me_2SiCl_2 (7.7 ml, 63 mmol) was added to the above reactant mixture dropwise at 0 °C. The mixture was allowed to warm to room temperature, stirred overnight and then filtered to remove precipitated LiCl. Evaporation of volatiles led to the title compound in 71% yield as a colourless viscous oil, which crystallized on standing. ^{1}H NMR ($CDCl_3$): δ −0.08 (m, 6H, Si*Me*$_2$), 1.28 (d, 3H, C*H*$_3$), 1.36 (d, 3H, C*H*$_3$), 4.07 (m, 2H, C*H*), 7.19–7.35 (m, 10H, *Ph*). ^{13}C NMR ($CDCl_3$): δ 1.6 (Si*Me*$_2$), 30.4 (CH_3), 53.1 (CH), 128.2 (C_{para}), 128.5 (C_{ortho}), 130.5 (C_{meta}), 151.8 (C_{ipso}). Anal. Found: C, 72.08; H, 8.65; N, 9.43. Calc. for $C_{18}H_{26}N_2Si$: C, 72.43; H, 8.78; N, 9.38%.

$[Me_2Si\{NLiCH(CH_3)Ph\}_2]_2$ (**1**)

A solution of Li^{n}Bu in hexane (4.86 mmol) was added dropwise to a stirred solution of $Me_2Si[NHCH(CH_3)Ph]_2$ (0.73 g, 2.43 mmol) in hexane (25 ml) at 0 °C. The pale yellow solution was allowed to warm to room temperature and stirred for 12 h. The reactant mixture was concentrated *in vacuo* to ∼10 ml and stored at −15 °C, yielding colourless crystals of **1** (0.68 g, 90%) that are suitable for a single-crystal X-ray diffraction analysis. ^{1}H NMR (C_6D_6): δ 0.22 (s, 6H, Si*Me*$_2$), 1.14 (d, 6H, C*H*$_3$), 4.26 (m, 2H, C*H*), 6.98–7.37 (m, 10H, *Ph*). ^{13}C NMR (C_6D_6): δ 6.5 (Si*Me*$_2$), 30.3 (CH_3), 58.3 (CH), 127.1 (C_{para}), 129.5 (C_{ortho}), 133.3 (C_{meta}), 154.8 (C_{ipso}). ^{7}Li NMR (C_6D_6): δ 1.18. Anal. Found: C, 68.95; H, 7.77; N, 8.85. Calc. for $C_{36}H_{48}Li_4N_4Si_2$: C, 69.66; H, 7.79; N, 9.03%.

$[\{Me_2Si\{NCH(CH_3)Ph\}_2\}ZrCl_2LiCl(OEt_2)_2]_2$ (**2**)

$ZrCl_4$ (1.12 g, 4.78 mmol) was added in small portions to a stirred solution of **1** (1.49 g, 4.78 mmol) in Et_2O (25 ml) at −78 °C. The red solution was warmed to room temperature and stirred for 12 h. The reactant mixture was filtered to remove precipitated LiCl. The filtrate was concentrated under vacuum and stored at −15 °C, yielding colourless crystals of compound **2** (2.5 g, 80%) that are suitable for a single-crystal X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$): δ −0.16 (m, 6H, Si*Me*$_2$), 1.23 (t, 12H, Et_2O), 1.76 (d, 6H, C*H*$_3$), 3.52 (q, 8H, Et_2O), 4.73 (m, 2H, C*H*), 7.17–7.39 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 3.5 (Si*Me*$_2$), 17.6 (Et_2O), 30.6 (CH_3), 64.4 (CH), 68.3 (Et_2O), 129.0 (C_{para}), 129.3 (C_{ortho}), 130.5 (C_{meta}), 149.7 (C_{ipso}). ^{7}Li NMR ($CDCl_3$): δ −0.38, −1.03. Anal. Found: C, 48.02; H, 6.82; N, 4.43. Calc. for $C_{52}H_{88}Cl_6Li_2N_4O_4Si_2Zr_2$: C, 48.10; H, 6.83; N, 4.31%.

$[\{Me_2Si\{NCH(CH_3)Ph\}_2\}HfCl_2LiCl(OEt_2)_2]_2$ (**3**)

Compound **3** was synthesized using a similar procedure to that of compound **2** (yield 90%). ^{1}H NMR ($CDCl_3$): $\delta - 0.22$ (m, 6H, Si*Me*$_2$), 1.27 (t, 12H, Et_2O), 1.72 (d, 6H, C*H*$_3$), 3.61 (q, 8H, Et_2O), 4.91 (m, 2H, C*H*), 7.14–7.41 (m, 10H, Ph). ^{13}C NMR

Table 4. Crystallographic data for compounds **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{36}H_{48}Li_4N_4Si_2$	$C_{52}H_{88}Cl_6Li_2N_4O_4Si_2Zr_2$	$C_{52}H_{88}Cl_6Hf_2Li_2N_4O_4Si_2$
Crystal system, space group	Tetragonal, $P\bar{4}2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions			
a (Å)	10.7384(15)	11.632(3)	11.6502(19)
b (Å)	10.7384(15)	12.380(3)	12.395(2)
c (Å)	15.734(3)	13.223(3)	13.133(2)
α (°)	90	98.699(4)	98.455(2)
β (°)	90	102.889(4)	102.690(2)
γ (°)	90	111.383(4)	111.846(2)
V(Å^3)	1814.3(5)	1670.8(7)	1661.6(5)
Z	2	1	1
D_{calc} (mg mm^{-3})	1.136	1.29	1.472
Absorption coefficient (mm^{-1})	0.127	0.628	3.44
F (000)	664	676	740
Crystal size (mm^3)	0.40 × 0.30 × 0.30	0.30 × 0.20 × 0.10	0.20 × 0.20 × 0.10
θ range for data collection (°)	2.30 to 25.02	1.63 to 25.00	1.64 to 25.00
Limiting indices	$-9 \le h \le 12, -12 \le k \le 12, -17 \le l \le 18$	$-13 \le h \le 13, -9 \le k \le 14, -15 \le l \le 12$	$-13 \le h \le 11, -14 \le k \le 13, -14 \le l \le 15$
Reflections collected	6859	6919	6880
Independent reflections	1602 ($R_{int} = 0.0284$)	5769 ($R_{int} = 0.0379$)	5723 ($R_{int} = 0.0193$)
Completeness to $\theta = 25°$ (%)	99.90	97.90	97.90
GOF	1.159	0.888	0.937
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0517, wR_2 = 0.1434$	$R_1 = 0.0596, wR_2 = 0.0717$	$R_1 = 0.0342, wR_2 = 0.0642$
R indices (all data)	$R_1 = 0.0535, wR_2 = 0.1450$	$R_1 = 0.1078, wR_2 = 0.0774$	$R_1 = 0.0409, wR_2 = 0.0660$

($CDCl_3$): δ 2.8 (Si*Me*$_2$), 17.4 (Et_2O), 30.8 (CH_3), 62.6 (*C*H), 68.3 (Et_2O), 128.8 (C_{para}), 129.4 (C_{ortho}), 130.4 (C_{meta}), 150.9 (C_{ipso}). ^{7}LiNMR($CDCl_3$): δ−0.32, −0.84. Anal. Found: C, 41.98; H, 5.98; N, 3.59. Calc. for $C_{52}H_{88}Cl_6Hf_2Li_2N_4O_4Si_2$: C, 42.40; H, 6.02; N, 3.80%.

X-ray crystallography

Diffraction data were collected on a Smart Apex CCD diffractometer using monochromated Mo Kα radiation, λ 0.710 73 Å at 183(2) K. Crystals were coated in oil and then mounted directly on the diffractometer under a stream of cold nitrogen gas. The structures were refined on all F^2 using SHELXL-97.[21] Non-hydrogen atoms were subjected to anisotropic refinement. A summary of the crystal data is given in Table 4. The CCDC reference numbers are 264 628, 264 629 and 264 630 for compounds **2, 1** and **3** respectively.

Acknowledgements

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REFERENCES

1. Kempe R. *Angew. Chem. Int. Ed.* 2000; **39**: 469.
2. Schattenmann FJ, Schrock RR, Davis WM. *Organometallics* 1998; **17**: 989.
3. Baumann R Davis WM, Schrock RR. *J. Am. Chem. Soc.* 1997; **119**: 3830.
4. Brand H, Capriotti JA, Arnold J. *Organometallics* 1994; **13**: 4469.
5. Uhrhammer R, Black DG, Gardner TG, Olsen JD, Jordan RF. *J. Am. Chem. Soc.* 1993; **115**: 8493.
6. Tjaden EB, Swenson DC, Jordan RF. *Organometallics* 1995; **14**: 371.
7. Cozzi PG, Gallo E, Floriani C, Chiesi-Villa A, Rizzoli C. *Organometallics* 1995; **14**: 4994.
8. Walther D, Fischer R, Görls H, Koch J, Schweder B. *J. Organometal. Chem.* 1996; **508**: 13.
9. Herskovics-Korine D, Eisen MS. *J. Organometal. Chem.* 1995; **503**: 307.
10. Flores JC, Chien JCW, Rausch RD. *Organometallics* 1995; **14**: 1827.
11. Gómez R, Green MLH, Haggitt JL. *J. Chem. Soc. Dalton Trans.* 1996; 939.
12. Gómez R, Duchateau R, Chernega AN, Teuben JH, Edelmann FT, Green MLH. *J. Organometal. Chem.* 1995; **491**: 153.
13. Gómez R, Green MLH, Haggitt JL. *J. Chem. Soc. Chem. Commun.* 1994; 2607.
14. De Boer EJM, de Boer HJR, Heeres HJ (Shell). *World Pat. Appl.* 95/04 087, 1995.
15. Hakala K, Löfgren B, Polamo M, Leskelä M. *Macromol. Rapid Commun.* 1997; **18**: 635.
16. Fuhrmann H, Brenner S, Arndt P, Kempe R. *Inorg. Chem.* 1996; **35**: 6742.

17. Oberthür M, Arndt P, Kempe R. *Chem. Ber.* 1996; **129**: 1087.
18. Nagy S, Krishnamurti R, Tyrell JA, Cribbs LV, Cocoman M (Occidental). *World Pat. Appl.* WO 96:33 202, 1996.
19. Horton AD, de With J. *Organometallics* 1997; **16**: 5424.
20. Hill MS, Hitchcock PB. *Organometallics* 2002; **21**: 3258 and references cited therein.
21. Sheldrick GM. SHELXTL 5.10 for Windows NT: structure determination software programs. Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.