

Synthesis and structures of some intermetallic compounds of gallium and indium [☆]

Alan H. Cowley ^{*,a}, Andreas Decken ^a, Nicholas C. Norman ^b, Rodney D. Schluter ^a,
Beth A. Walden ^a

^a Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA

^b Department of Chemistry, The University of Newcastle Upon Tyne, Newcastle Upon Tyne, NE1 7RU, UK

Received 8 April 1995

Abstract

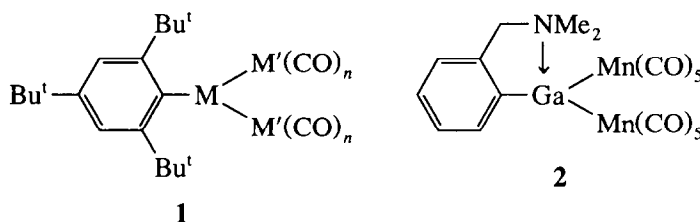
The reaction of sonochemically prepared “GaI” with one equivalent of $\text{Co}_2(\text{CO})_8$ afforded the intermetallic compound $[\text{Ga}(\text{THF})(\text{Co}(\text{CO})_4)_2]$ (**5**). Treatment of **5** with $\text{Ar}^* \text{Li}$ ($\text{Ar}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$) resulted in $[\text{Ga}(\text{Ar}^*)(\text{Co}(\text{CO})_4)_2]$ (**6**). The structures of **5** and the analogous indium compound, $[\text{InCl}(\text{THF})(\text{Co}(\text{CO})_4)_2]$ (**7**) have been established by X-ray crystallography.

Keywords: Gallium; Indium; Cobalt; Intermetallics; Crystal structures

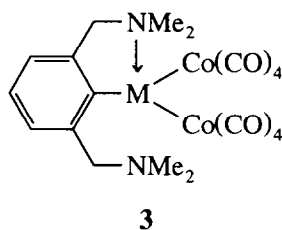
1. Introduction

Intermetallic phases such as $\beta\text{-CoGa}$ and $\varepsilon\text{-NiIn}$ find application as, for example, Schottky barriers and ohmic contacts [1]. This relevance to materials science has prompted a surge of interest in novel organometallic approaches to the foregoing and related phases [2]. In terms of single-source MOCVD precursors, most of the emphasis has been placed on compounds that feature a transition metal / Group 13 element ratio of 1:1. However, in related work on single-source precursors to GaAs [3], it has become apparent that precursors with different stoichiometries can produce phases of 1:1 stoichiometry as a consequence of facile elimination reactions. We have therefore turned our attention to the synthesis and structural assay of homoleptic derivatives

such as $[\text{Ga}\{\text{Mn}(\text{CO})_5\}_3]$ [4] and a range of compounds with 2:1 stoichiometry as exemplified below [5–7].



$\text{M} = \text{Ga}$ or In ; $\text{M}' = \text{Co}$, $n = 4$; $\text{M}' = \text{Mn}$, $n = 5$



$\text{M} = \text{Ga}$ or In

In each of the foregoing cases, the synthesis of the desired intermetallic compound was effected by a salt elimination reaction between the appropriate alkali metal carbonylate and Group 13 halide derivative. In the

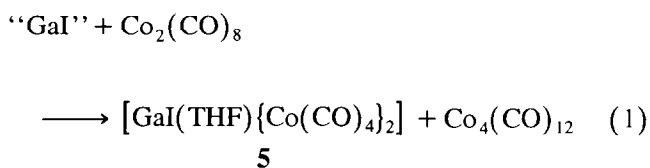
[☆] This paper is dedicated to Professor Dr. Herbert Schumann on the occasion of his 60th birthday in recognition of his many contributions to organometallic and inorganic chemistry.

* Corresponding author.

present paper, we have adopted a different synthetic strategy, namely the insertion of sonochemically prepared gallium(I) iodide into a cobalt–cobalt bond. These efforts resulted in the new compound $[\text{GaI}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**5**) which can be converted into the known compound $[\text{Ga}(\text{Ar}^*)\{\text{Co}(\text{CO})_4\}_2]$ (**6**) by reaction with $\text{Ar}^* \text{Li}$ ($\text{Ar}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$). Compound **5** has been characterized by X-ray crystallography; the X-ray structure of $[\text{InCl}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**7**) is also reported.

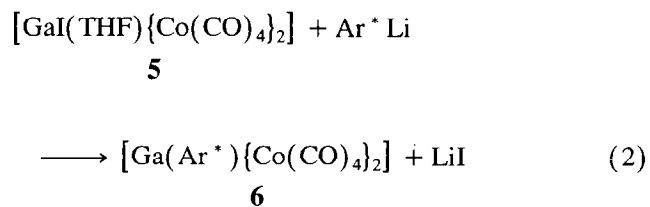
2. Results and discussion

The gallium subiodide “GaI” (**4**) was prepared sonochemically following the procedure of Green et al. [8]. Treatment of **4** with dicobalt octacarbonyl in THF solution at -40°C afforded a 27% yield of $[\text{GaI}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**5**) as indicated in Eq. (1):



Compound **5** was separated from $\text{Co}_4(\text{CO})_{12}$ on the basis of the significantly higher solubility of the former. Well-shaped amber crystals of **5** were obtained by recrystallization from THF; however, this compound is soluble in most organic solvents. Mass spectroscopy proved to be a useful technique for the identification of **5** on account of the characteristic isotopic abundance pattern for ^{69}Ga (60%) and ^{71}Ga (40%). Thus, **5** exhibits a low-intensity peak at $m/z = 611$ corresponding to the $\text{M}^+ + \text{H}$ ion. The presence of a higher-intensity peak at $m/z = 411$ is attributable to the loss of THF and an iodine atom and thus indicative of the ease of solvent removal. Confirmation of the identity of **5** was provided by a single-crystal X-ray diffraction study (vide infra).

Treatment of **5** with $\text{Ar}^* \text{Li}$ ($\text{Ar}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$) resulted in a 22% yield of the metathesis product **6**, as summarized in Eq. (2):



We have prepared **6** previously via the reaction of $\text{Ar}^* \text{GaCl}_2$ with $\text{NaCo}(\text{CO})_4$ in Et_2O solution [5]. The spectral properties of **6** are identical to those described previously. The indium derivative $[\text{InCl}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ was synthesized according to the literature

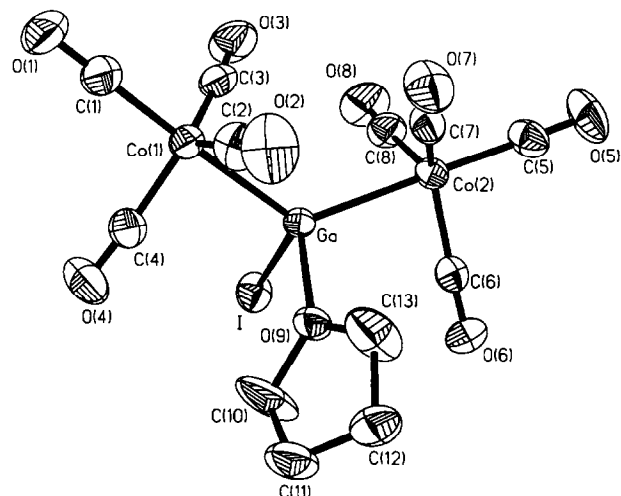


Fig. 1. View and atom numbering scheme for $[\text{GaI}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**5**). Thermal ellipsoids are at the 30% probability level.

method [9] and recrystallized from pentane. Compound **7** was characterized on the basis of mass spectroscopy and elemental analysis.

Compound **5** crystallizes in the space group $P\bar{1}$ with two molecules per unit cell and there are no unusually short intermolecular contacts. The gallium atom is four-coordinate and the coordination sphere comprises two tetracarbonylcobaltate moieties, a chloride ligand, and a coordinated THF molecule (Fig. 1). The overall symmetry of the array is approximately tetrahedral; however, there is a wide disparity in the bond angles which range from $97.6(2)^\circ$ ($\text{I}-\text{Ga}-\text{O}(9)$) to $124.7(1)^\circ$ ($\text{Co}(1)-\text{Ga}-\text{Co}(2)$). Presumably the obtuse nature of the latter angle is due to the minimization of steric interactions between the $\text{Co}(\text{CO})_4$ groups. Such a trend has been observed previously for $[\text{InCl}(\text{THF})\{\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)\}_2]$ and related complexes [10]. The Ga–Co bond lengths are approximately equal, and the average bond length of $2.447(2)$ Å falls within the range of 2.38–2.58 Å that has been reported for the few compounds that feature this linkage [2b,11]. The bond length between the donor oxygen atom and gallium is $2.054(5)$ Å which is comparable to those in related adducts. Interestingly, the indium analogue $[\text{InCl}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**7**) is not isomorphous with **5**. Molecules of **7** crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$ (Fig. 2). However, as in the case of **5**, there are no unduly short intermolecular interactions. Moreover, the overall geometry and metrical parameters at the Group 13 center are very similar for **5** and **7**. Thus, the bond angles at the approximately tetrahedral indium atom range from $94.4(2)^\circ$ ($\text{Cl}-\text{In}-\text{O}(9)$) to 131.1° ($\text{Co}(1)-\text{In}-\text{Co}(2)$). The two In–Co bond distances are similar and the average value of $2.567(2)$ Å is comparable to those in, for example, $[\text{In}\{(2,6\text{-Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\{\text{Co}(\text{CO})_4\}_2]$ ($2.676(1)$ Å) [6], $[\text{In}(\text{CH}_2\text{SiMe}_3)(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ ($2.6343(4)$ Å) [2b], $[\text{InCl}_2\{\text{Co}(\text{CO})_4\}_2]^-$ ($2.614(4)$ Å)

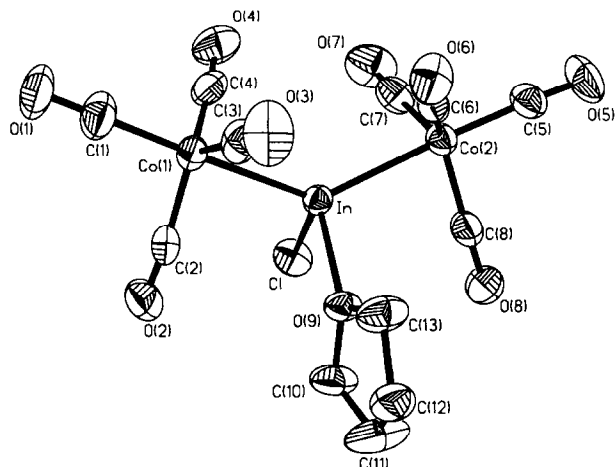


Fig. 2. View and atom numbering scheme for $[\text{InCl}(\text{THF})(\text{Co}(\text{CO})_4)_2]$ (7). Thermal ellipsoids are at the 30% probability level.

$[\text{12}]$, $[\text{In}[\text{Co}(\text{CO})_4)_3]^-$ (2.705(1) Å) [13], and $[\text{In}(\text{Ar}^*)-\text{Co}(\text{CO})_4)_2]$ (2.631(1) Å) [4].

3. Experimental details

All manipulations were carried out under dry argon using standard Schlenk techniques or in an HE-493 Vacuum Atmospheres drybox. Unless otherwise stated, all solvents were dried over sodium and distilled from

sodium benzophenone ketyl under argon prior to use. Dicobalt octacarbonyl was purchased from Strem and used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA. IR spectra were obtained in pentane solution on a Digilab FTS-40 spectrophotometer. Sonications were run on a Misonix XL 2015 ultrasonic processor, 475 W power output. NMR spectra were obtained on a GE QE-300 spectrometer (^1H 300.17 MHz; ^{13}C 75.48 MHz) and are referenced to C_6D_6 which was dried over Na/K alloy and distilled prior to use. Mass spectra (CI) were run on a Finnigan MAT 4023 instrument and (uncorrected) melting points were obtained in sealed glass capillaries under argon (1 atm).

3.1. Preparation of "Gal" (4)

Gallium metal (0.74 g, 10.61 mmol) and diiodine (1.35 g, 5.30 mmol) were dissolved in 50 ml of toluene and placed in a Suslick cell which had been modified by attachment of a Schlenk arm. A powdery precipitate of "Gal" was formed after the reaction mixture had been sonicated for 4 min at 60% power output.

3.2. Preparation of $[\text{Gal}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (5)

The toluene suspension of "Gal" described above was added via Teflon cannula to a solution of 3.42 g

Table 1
Crystal data, data collection, and refinement of the structures of 5 and 7

Compound	5	7
Formula	$\text{C}_{12}\text{H}_8\text{Co}_2\text{GaI}_2\text{O}_9$	$\text{C}_{12}\text{H}_8\text{Co}_2\text{ClInO}_9$
Formula weight	610.7	564.3
Crystal system	triclinic	monoclinic
Crystal size (mm)	$0.13 \times 0.19 \times 0.19$	$0.19 \times 0.25 \times 0.45$
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.545(2)	11.611(2)
b (Å)	10.948(2)	11.002(2)
c (Å)	12.823(2)	15.268(2)
α (deg)	89.60(3)	
β (deg)	78.50(3)	99.46(2)
γ (deg)	70.96(3)	
V (Å ³)	979.2(5)	1923(1)
Z	2	4
d_{calc} (g cm ⁻³)	2.071	1.948
μ (cm ⁻¹)	465.4	30.70
Index ranges	$0 < h < 8, -12 < k < 13$ $-14 < l < 15$	$0 < h < 13, 0 < k < 13$ $-18 < l < 17$
Scan range (deg)	4.0–50.0	4.0–50.0
Independent reflections	3411	3375
Reflections observed	2515	1953
Absorption correction	SHELXA	N/A
Min./Max. trans.	0.25711/0.71096	
Parameters refined	227	227
R/R_w (%)	4.46, 5.10	4.77, 5.06
w	0.0005	0.0008
S	1.51	1.08
$R = \Sigma(F_o - F_c) / \Sigma F_o , R_w = [\Sigma w(F_o - F_c)^2 / \Sigma F_o^2]^{1/2}$		

(10.0 mmol) of $\text{Co}_2(\text{CO})_8$ in 30 ml of THF at -40°C . The cold bath was removed after 20 min, and the solution allowed to warm to room temperature. Solvent removal, followed by fractional crystallization from THF afforded rod-shaped amber crystals of **5**. Yield 1.67 g (27%). M.p. $157\text{--}158^\circ\text{C}$. MS (CI, CH_4): 611 ($\text{M}^+ + \text{H}$); 483 ($\text{M}^+ - \text{I}$) 411 ($\text{M}^+ - \text{THF} - \text{I}$). IR: ν_{max} (CO) 2109w, 2100s, 2080s, 2009s cm^{-1} .

3.3. Preparation of $[\text{Ga}(\text{Ar}^*)\{\text{Co}(\text{CO})_4\}_2]$ ($\text{Ar}^* = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$) (**6**)

A solution of 0.35 g (1.38 mmol) of $\text{Ar}^* \text{Li}$ in 30 ml of THF was added by means of a cannula to a solution of 0.80 g (1.31 mmol) of **5** in 30 ml of THF. The reaction mixture was stirred at room temperature for 12 h, following which the solvent was removed under vacuum. Yellow microcrystalline **6** was obtained after recrystallization from hexane. Yield 0.3 g (35%). The spectroscopic properties of **6** were identical to those of a sample of **6** prepared by a different route [5].

3.4. Preparation of $[\text{InCl}(\text{THF})\{\text{Co}(\text{CO})_4\}_2]$ (**7**)

This compound was prepared according to the literature method [9].

3.5. X-ray crystallography

Suitable single crystals of **5** and **7** were obtained by recrystallization from THF and pentane solutions, re-

Table 2
Positional parameters for **5**

Atom	x/a	y/b	z/c	U_{eq}
Ga	7593(1)	2602(1)	2480(1)	49(1)
I	4332(1)	2978(1)	3774(1)	78(1)
Co(1)	7298(2)	2446(1)	615(1)	64(1)
Co(2)	10151(1)	1145(1)	3238(1)	56(1)
C(1)	7072(17)	2238(9)	-727(9)	98(5)
C(2)	9291(16)	2966(10)	284(8)	88(5)
C(3)	7432(14)	856(9)	972(7)	82(4)
C(4)	5099(14)	3708(9)	1014(7)	76(4)
C(5)	12158(14)	114(9)	3765(7)	79(4)
C(6)	9249(12)	2361(8)	4312(7)	71(4)
C(7)	11653(13)	1258(8)	2008(8)	73(4)
C(8)	8813(14)	40(8)	3317(7)	78(4)
C(10)	6224(17)	5594(9)	2927(16)	179(10)
C(11)	6992(14)	6661(8)	2900(10)	102(5)
C(12)	9043(15)	6032(9)	2923(10)	101(5)
C(13)	9482(15)	4710(10)	2568(13)	127(7)
O(1)	6931(15)	2111(8)	-1575(6)	146(5)
O(2)	10570(13)	3326(9)	10(7)	128(5)
O(3)	7492(14)	-176(7)	1144(6)	123(5)
O(4)	3690(10)	4553(7)	1197(6)	109(3)
O(5)	13426(11)	-522(8)	4066(7)	123(4)
O(6)	8699(11)	3085(7)	5018(6)	112(4)
O(7)	12700(10)	1269(8)	1240(6)	108(4)
O(8)	8058(12)	-692(7)	3400(7)	114(4)
O(9)	7761(7)	4420(4)	2672(4)	64(2)

Table 3
Positional parameters for **7**

Atom	x/a	y/b	z/c	U_{eq}
In	2506(1)	1919(1)	387(1)	52(1)
Co(1)	4327(1)	2757(1)	-172(1)	67(1)
Co(2)	2244(1)	73(1)	1351(1)	61(1)
Cl	865(3)	2076(3)	-784(2)	86(1)
C(1)	5564(11)	3272(14)	-625(9)	101(6)
C(2)	3315(11)	3911(12)	-611(8)	81(5)
C(3)	4974(10)	2891(11)	973(9)	79(5)
C(4)	4234(10)	1315(14)	-666(8)	82(5)
C(5)	1982(10)	-1199(11)	2021(8)	80(5)
C(6)	3576(10)	520(10)	1987(7)	64(4)
C(7)	2260(11)	-735(10)	353(9)	86(5)
C(8)	957(11)	862(11)	1463(8)	85(5)
C(10)	981(11)	4283(11)	890(8)	97(6)
C(11)	771(14)	4906(16)	1672(11)	141(8)
C(12)	1817(14)	4821(12)	2339(8)	105(7)
C(13)	2448(11)	3768(11)	2065(7)	95(6)
O(1)	6331(8)	3596(11)	-923(7)	132(5)
O(2)	2742(9)	4676(9)	-917(7)	127(5)
O(3)	5426(9)	3023(10)	1683(6)	122(5)
O(4)	4258(9)	385(10)	-996(7)	117(5)
O(5)	1810(8)	-1960(9)	2475(7)	121(5)
O(6)	4428(7)	763(9)	2430(5)	99(4)
O(7)	2282(10)	-1319(10)	-256(7)	137(5)
O(8)	92(8)	1341(9)	1537(7)	121(5)
O(9)	1956(6)	3493(6)	1160(4)	67(3)

spectively. Both data crystals were mounted in thin-walled capillaries and sealed under argon. A summary of data collection and structure refinement is presented in Table 1. All diffraction measurements were carried out at 298 K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and employing the $2\theta - \theta$ scan mode. Accurate unit cell parameters for **5** and **7** were obtained by recentering 25 strong reflections in the range $24^\circ < 2\theta < 28^\circ$. The data sets for both compounds were corrected for Lorentz and polarization effects as well as absorption. The structures were solved by direct methods and refined by full-matrix least squares on F with Siemens SHELXTL-PLUS software [14].

Table 4
Selected bond length (\AA) and angles ($^\circ$) for **5** and **7**

5			
Ga-I	2.587(1)	Ga-Co(1)	2.458(2)
Ga-Co(2)	2.436(2)	Ga-O(9)	2.061(6)
I-Ga-Co(1)	111.1(1)	I-Ga-Co(2)	109.6(1)
Co(1)-Ga-Co(2)	124.7(1)	I-Ga-O(9)	97.6(2)
Co(1)-Ga-O(9)	103.9(2)	Co(2)-Ga-O(9)	106.1(2)
7			
In-Co(1)	2.576(2)	In-Co(2)	2.557(2)
In-Cl	2.396(3)	In-O(9)	2.247(7)
Co(1)-In-Co(2)	131.1(1)	Co(1)-In-Cl	108.8(1)
Co(2)-In-Cl	109.3(1)	Co-In-O(9)	102.6(2)
Co(2)-In-O(9)	103.8(2)	Cl-In-O(9)	94.4(2)

Acknowledgment

We are grateful to the National Science Foundation and the Robert A. Welch Foundation for generous financial support. We also thank NATO for an International Collaborative Research Grant.

References

- [1] (a) T.C. Kuo, T.W. Wang and K.L. Wang, *J. Cryst. Growth*, **111** (1991) 996; (b) T.C. Kuo, T.W. Wang, R. Arghvani, T. George and T.L. Lin, *J. Vac. Sci. Technol. B.*, **10** (1992) 1923; (c) F. Maury, L. Brandt and H.D. Kaesz, *J. Organomet. Chem.*, **449** (1993) 159.
- [2] (a) Y.-J. Chen, H.D. Kaesz, Y.K. Kim, H.-J. Müller, R.S. Williams and Z. Xue, *Appl. Phys. Lett.*, **55** (1989) 2760; (b) R.A. Fischer, J. Behm, T. Priermeier and W. Scherer, *Angew. Chem. Int. ed. Engl.* **32** (1993) 746; (c) R.A. Fischer, W. Scherer and M. Kleine, *Angew. Chem. Int. Ed. Engl.* **32**, (1993) 748.
- [3] A.H. Cowley and R.A. Jones, *Polyhedron*, **13** (1994) 1149, and references therein.
- [4] A.H. Cowley, A. Decken, C.A. Olazábal and N.C. Norman, *Z. Anorg. Allgem. Chem.*, in press.
- [5] A.H. Cowley, A. Decken, C.A. Olazábal and N.C. Norman, *Inorg. Chem.*, **33** (1994) 3435.
- [6] C.A. Olazábal, M.A. Thesis, University of Texas at Austin, 1994.
- [7] F.P. Gabbai, A.H. Cowley, C.A. Olazábal, C.J. Carrano, L.M. Mokry and M.R. Bond, *Organometallics*, **13** (1994) 621.
- [8] M.L.H. Green, P. Mountford, G.J. Smout and S.R. Speel, *Polyhedron*, **9** (1990) 2763.
- [9] D.J. Patmore and W.A.G. Graham, *Inorg. Chem.*, **5** (1966) 1586.
- [10] L.M. Clarkson, W. Clegg, D.C.R. Hockless, N.C. Norman, L.J. Farrugia, S.G. Bott and J.L. Atwood, *J. Chem. Soc. Dalton Trans.*, (1991) 2241.
- [11] R.A. Fischer, J. Behm and T. Priermeier, *J. Organomet. Chem.*, **429** (1992) 275.
- [12] L.M. Clarkson, K. McCrudden, N.C. Norman and L.J. Farrugia, *Polyhedron*, **9** (1991) 2533.
- [13] L.M. Clarkson, L.J. Farrugia and N.C. Norman, *Acta Cryst.*, **C47** (1991) 2525.
- [14] G.M. Sheldrick, *SHELXTL-PLUS* (PC) [4.2], Siemens Analytical X-ray Instruments, Inc., 1990.