

Synthesis and characterisation of the first auracyclobutane complex

Maarten B. Dinger, William Henderson *

Department of Chemistry, The University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received 1 October 1998

Abstract

The silver(I) oxide mediated reaction of the gold(III) dichloride complex $[\{C_6H_3(CH_2NMe_2)-2-(OMe)-5\}AuCl_2]$ with 1,1,3,3-tetracyanopropane, $CH(CN)_2CH_2CH(CN)_2$ in refluxing dichloromethane affords, in a high yield, the first example of an auracyclobutane complex, $[\{C_6H_3(CH_2NMe_2)-2-(OMe)-5\}Au\{C(CN)_2CH_2C(CN)_2\}]$. The X-ray crystal structure shows a slightly puckered auracyclobutane ring, with structural features similar to the known platinacyclobutane complex $[Pt\{C(CN)_2CH_2C(CN)_2\}(PPh_3)_2]$, which can also be synthesised by the silver(I) oxide method. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Gold; Metallacyclobutane; Crystal structure; Electrospray mass spectrometry

1. Introduction

Metallacyclobutane complexes are an extremely well-known class of compound, and many examples derived from main-group metals, transition-metals and actinides have been characterised, spurred on largely due to their application in the olefin metathesis reaction, in which they are considered key intermediates [1,2]. A number of reviews concerning metallacyclobutanes have been published [3–6], the last devoted solely to platinacycles. Indeed, platinacyclobutanes are archetypal metallacycles, first prepared in 1955 [7], with a plethora of additional examples, both of platinum(II) and platinum(IV), since prepared. Despite gold(III) being isoelectronic (d^8) with platinum(II), no auracyclobutane complexes have hitherto been reported. Examination of the literature reveals a dearth of four-membered auracycles generally.

We are currently investigating the metallacyclic chemistry of gold(III), and complexes (derived from the gold(III) dihalide $[Au\{C_6H_3(CH_2NMe_2)-2-(OMe)-$

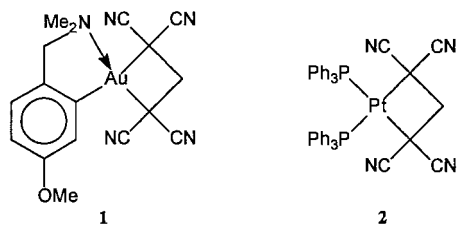
$5\}Cl_2]$ [8] containing $Au-C-C(O)-C$ (auracyclobutan-3-one) [9], $Au-C-S(O)_2-C$ (aurathietane-3,3-dioxide) [9] and $Au-N-C(O)-N$ (auraureylene) [10] ring systems have been prepared. Their ready formation, especially the auracyclobutan-3-one complex, suggested that the previously unknown auracyclobutane ring system should be readily accessible; in this paper we report the synthesis of the first auracyclobutane complex.

2. Results and discussion

When $[Au\{C_6H_3(CH_2NMe_2)-2-(OMe)-5\}Cl_2]$, 1,1,3,3-tetracyanopropane and silver(I) oxide were refluxed in dichloromethane for 3 h, complex **1** (containing the unprecedented auracyclobutane ring system) could be isolated as colourless needles. The analogous (and known) [11,12] platinum(II) complex **2** could be similarly prepared from *cis*- $[PtCl_2(PPh_3)_2]$, 1,1,3,3-tetracyanopropane and silver(I) oxide. While silver(I) oxide has been used for the synthesis of a wide range of metallacyclic complexes [13], including gold(III) complexes [9,10], this is the first report of the synthesis of a metallacyclobutane complex using this methodology.

* Corresponding author. Fax: +647-838-4219.

E-mail address: w.henderson@waikato.ac.nz (W. Henderson)



In order to fully characterise **1**, assess its bonding, and compare this with the structure of the analogous platinum(II) example **2** [12], a single-crystal X-ray structure determination was carried out. The molecular structure of the complex is given in Fig. 1, together with the atom numbering scheme, while Table 1 gives bond lengths and angles for the structure. The complex contains the expected four-membered metallacyclobutane ring, analogous to the platinum complex **2**, to which this structure overall bears a remarkable similarity. The auracyclobutane ring is puckered (see inset to Fig. 1) with a fold angle of $20.1(6)^\circ$, statistically identical to that of **2**, for which an angle of $20.1(5)^\circ$ was measured [12]. The puckering of the ring appears to be a solid state effect only, with the room temperature (r.t.) ^1H - and ^{13}C -NMR spectra showing only single resonances for the methylene (both for the cycloaurated

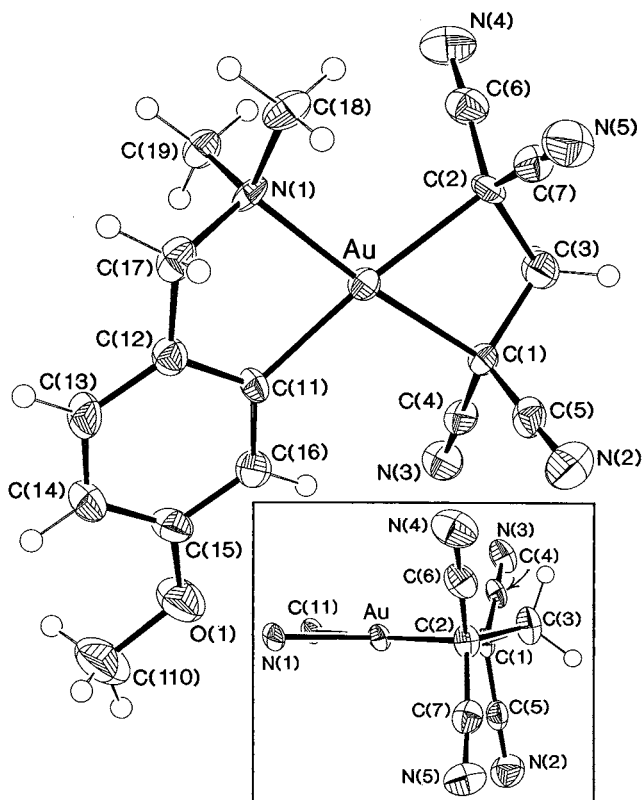


Fig. 1. Molecular structure of $[\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)\text{-}2\text{-(OMe)-}5\}\text{Au}\{\text{C}(\text{CN})_2\text{CH}_2\text{C}(\text{CN})_2\}] \cdot \text{CHCl}_3$, illustrating the atom numbering scheme. The inset shows a side view of the structure, with only the Au-bonded atoms of the benzylamine ligand shown, showing the non-planarity of the auracyclobutane ring.

Table 1

Bond lengths (Å) and bond angles ($^\circ$) for $1 \cdot \text{CHCl}_3$, with estimated standard deviations in parentheses

| Bond lengths (Å) | | | |
|--------------------------|----------|-------------------|-----------|
| Au(1)–C(11) | 2.065(5) | C(1)–C(3) | 1.556(8) |
| Au(1)–C(1) | 2.109(5) | C(2)–C(6) | 1.452(9) |
| Au(1)–N(1) | 2.118(4) | C(2)–C(7) | 1.452(9) |
| Au(1)–C(2) | 2.185(5) | C(2)–C(3) | 1.584(8) |
| O(1)–C(15) | 1.382(8) | C(11)–C(16) | 1.392(8) |
| O(1)–C(110) | 1.440(9) | C(11)–C(12) | 1.409(8) |
| N(1)–C(17) | 1.505(8) | C(12)–C(13) | 1.393(9) |
| N(1)–C(19) | 1.498(7) | C(12)–C(17) | 1.508(8) |
| N(1)–C(18) | 1.514(8) | C(13)–C(14) | 1.399(10) |
| N(2)–C(5) | 1.151(8) | C(14)–C(15) | 1.383(9) |
| N(3)–C(4) | 1.146(8) | C(15)–C(16) | 1.394(8) |
| N(4)–C(6) | 1.157(9) | N(5)–C(7) | 1.153(8) |
| C(21)–Cl(2) | 1.740(8) | C(1)–C(4) | 1.456(8) |
| C(21)–Cl(3) | 1.746(8) | C(1)–C(5) | 1.468(8) |
| C(21)–Cl(1) | 1.774(8) | | |
| Bond angles ($^\circ$) | | | |
| C(11)–Au(1)–C(1) | 104.5(2) | C(3)–C(2)–Au(1) | 90.8(3) |
| C(11)–Au(1)–N(1) | 81.2(2) | C(1)–C(3)–C(2) | 101.9(5) |
| C(1)–Au(1)–N(1) | 174.0(2) | N(3)–C(4)–C(1) | 178.5(6) |
| C(11)–Au(1)–C(2) | 173.4(2) | N(2)–C(5)–C(1) | 178.8(7) |
| C(1)–Au(1)–C(2) | 69.2(2) | N(4)–C(6)–C(2) | 177.0(7) |
| N(1)–Au(1)–C(2) | 105.2(2) | N(5)–C(7)–C(2) | 177.0(7) |
| C(15)–O(1)–C(110) | 119.5(6) | C(16)–C(11)–C(12) | 120.2(5) |
| C(17)–N(1)–C(19) | 110.5(5) | C(16)–C(11)–Au(1) | 126.6(4) |
| C(17)–N(1)–C(18) | 108.5(5) | C(12)–C(11)–Au(1) | 113.0(4) |
| C(19)–N(1)–C(18) | 108.7(5) | C(13)–C(12)–C(11) | 119.5(6) |
| C(17)–N(1)–Au(1) | 107.6(3) | C(13)–C(12)–C(17) | 123.9(5) |
| C(19)–N(1)–Au(1) | 109.2(3) | C(11)–C(12)–C(17) | 116.6(5) |
| C(18)–N(1)–Au(1) | 112.3(4) | C(14)–C(13)–C(12) | 120.4(6) |
| C(4)–C(1)–C(5) | 110.2(5) | C(15)–C(14)–C(13) | 119.4(6) |
| C(4)–C(1)–C(3) | 115.5(5) | O(1)–C(15)–C(14) | 124.8(6) |
| C(5)–C(1)–C(3) | 112.5(5) | O(1)–C(15)–C(16) | 113.8(6) |
| C(4)–C(1)–Au(1) | 115.0(4) | C(14)–C(15)–C(16) | 121.3(6) |
| C(5)–C(1)–Au(1) | 108.2(4) | C(15)–C(16)–C(11) | 119.3(5) |
| C(3)–C(1)–Au(1) | 94.5(3) | N(1)–C(17)–C(12) | 108.9(5) |
| C(6)–C(2)–C(7) | 112.3(5) | C(6)–C(2)–C(3) | 113.4(5) |
| Cl(2)–C(21)–Cl(3) | 111.6(5) | C(7)–C(2)–C(3) | 115.7(5) |
| Cl(2)–C(21)–Cl(1) | 109.2(4) | C(6)–C(2)–Au(1) | 114.5(4) |
| Cl(3)–C(21)–Cl(1) | 110.7(4) | C(7)–C(2)–Au(1) | 108.2(4) |

and metallacyclobutane rings) and *N,N*-dimethylamine groups.

As expected for a d^8 metal centre, the gold atom is coordinated in a distorted square-planar arrangement, with the four- and five-membered metallacycles in the plane. The main distortion is the C(1)–Au–C(2) bite angle of $69.2(2)^\circ$, not significantly different to the $68.4(2)^\circ$ bite angle reported for **2**. The geometry about the central gold atom is planar, with a maximum deviation from the least-squares plane drawn through N(1), C(11), Au, C(1) and C(2) being $0.038(3)$ Å, for C(1). Additionally, the Au–C(1) and Au–C(2) bond lengths are not equal, as expected on *trans*-influence grounds [14], with the latter ($2.185(5)$ Å) longer than the former ($2.109(5)$ Å), attributable to C(11) having a higher *trans*-influence than N(1). The average bond distance of $2.147(7)$ Å is, again, not significantly differ-

ent to the average distance observed for **2** (2.138(8) Å). A final note of interest is the chloroform solvate, which, with a C...N(4) contact of 3.346(8) Å (H...N(4) 2.447(8) Å), forms a weak hydrogen-bond to a cyano group.

The positive-ion electrospray mass spectrum of **1** in MeCN/H₂O shows very strong ions for [M + NH₄]⁺ and [2M + NH₄]⁺ at *m/z* 525 and 1024, respectively. The former remains the principal ion even at a very high cone voltage of 200 V. This very high stability is attributed to the presence of two metallacycles, and has been observed previously in other gold(III) complexes with dual ring systems [10,15]

In summary, we have synthesised the first stable metallacyclobutane complex of gold; this preliminary research paves the way for an in-depth study of the synthesis, structures and reactivities of auracyclobutane complexes and comparisons with the extensive series of platinum(II) analogues.

3. Experimental

Melting points were measured in air on a Reichert hotstage apparatus and are uncorrected. IR spectra were recorded as KBr discs on a BioRad FTS-40 spectrophotometer. Electrospray mass spectra were recorded in positive-ion mode on a VG Platform II instrument, using a 1:1 mixture of MeCN/H₂O as the mobile phase. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago.

Unambiguous NMR assignment was achieved by a combination inverse 2D NMR experiments (HSQC, Heteronuclear Single Quantum Coherence and HMBC, Heteronuclear Multiple Bond Correlation), and were recorded on a Bruker DRX 400 spectrometer at 400.13 and 100.61 MHz for the proton and carbon channels, respectively, chemical shifts relative to SiMe₄ (δ 0.0). The ¹H- and ¹³C-¹H-NMR spectra were recorded on either the instrument above, or on a Bruker AC300 spectrometer at 300.13 and 75.47 MHz, respectively.

All syntheses were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and freshly distilled prior to use. The compound [Au{C₆H₃(CH₂NMe₂)-2-(OMe)-5}Cl₂] [**8**] was prepared as reported, by transmetallation of the orthomercurated complex [Hg{C₆H₃(CH₂NMe₂)-2-(OMe)-5}Cl] [**16**] with Me₄NAuCl₄. The complex *cis*-[PtCl₂(PPh₃)₂] was prepared from [PtCl₂(1,5-cyclo-octadiene)] [**17**] and 2 M equivalents of PPh₃ in dichloromethane. The compound 1,1,3,3-tetracyanopropane (Aldrich) was used as supplied.

3.1. Synthesis of auracyclobutane complex **1**

To a Schlenk flask containing dichloromethane (25 ml) that had previously been degassed and flushed with nitrogen, was added [Au{C₆H₃(CH₂NMe₂)-2-(OMe)-5}Cl₂] (0.070 g, 0.162 mmol), 1,1,3,3-tetracyanopropane (0.024 g, 0.1667 mmol) and silver(I) oxide (0.183 g, excess). The resulting mixture was refluxed under nitrogen for 3 h, during which time the solution became bright green. With no further efforts at excluding air, the silver salts were filtered off and the solvent removed under reduced pressure, to leave a green oil. Addition of a small quantity of chloroform rapidly (ca. 5 min) induced the formation of beige crystals (0.062 g), which by ¹H- and ¹³C-NMR spectroscopy were determined to be of high purity. Subsequent recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution gave [Au{C₆H₃(CH₂NMe₂)-2-(OMe)-5}Au{C(CN)₂CH₂C(CN)₂}] as fine white needles (0.051 g, 63%). M.p. 110°C (decomposes without melting). Found: C, 40.62; H, 3.04; N, 13.88%; C₁₇H₁₆N₅OAu requires: C, 40.57; H, 3.20; N, 13.91%. IR [KBr disc, ν (CN region)]: 2218 (m) cm⁻¹. ¹H-NMR [CD₃S(O)CD₃, 400.13 MHz]: δ 7.36 (1H, *d*, ³J_{HH} = 8.30 Hz, C₁₃-H), 7.11 (1H, *d*, ⁴J_{HH} = 2.44 Hz, C₁₆-H), 6.98 (1H, *dd*, ³J_{HH} = 8.31 Hz, ⁴J_{HH} = 2.48 Hz, C₁₄-H), 4.51 (2H, *s*, CH₂NMe₂), 4.30 (2H, *s*, CCH₂C), 3.86 (3H, *s*, OCH₃), 3.17 (6H, *s*, NCH₃). ¹³C-NMR [CD₃S(O)CD₃, 75.47 MHz]: δ 157.2 (*s*, C₁₅), 149.3 (*s*, C₁₁), 139.6 (*s*, C₁₂), 124.1 (*d*, C₁₃), 118.5 [*s*, C(CN)₂ *trans* C], 117.0 [*s*, C(CN)₂ *trans* N], 114.3 (*d*, C₁₆), 113.2 (*d*, C₁₄), 112.8 [*s*, C(CN)₂ *trans* C], 102.6 [*s*, C(CN)₂ *trans* N], 71.6 (*t*, NCH₂), 55.1 (*t*, OCH₃), 50.5 (*q*, NCH₃), 41.7 (*t*, CCH₂C).

3.2. Synthesis of platinacyclobutane complex **2**

In a similar fashion to the synthesis of **1**, *cis*-[PtCl₂(PPh₃)₂] (0.101 g, 0.128 mmol), 1,1,3,3-tetracyanopropane (0.019 g, 0.132 mmol) and silver(I) oxide (0.162 g, excess) were added to dichloromethane (30 ml) and refluxed in a nitrogen atmosphere for 5 h. Filtration of the silver salts, and evaporation of the solvent gave a bright orange oil, which by ³¹P-NMR was approximately 80% pure. Purification proved difficult, but small quantities of [Pt{C(CN)₂CH₂C(CN)₂}(PPh₃)₂] could be obtained as white crystals (with spectroscopic features consistent with published values), together with flakes from a bright orange film. IR [KBr disc, ν (CN region)]: 2220 (m) cm⁻¹. Lit. [11] 2220 cm⁻¹. ³¹P-NMR (CDCl₃, 121.49 MHz): δ 12.4 [*s*, (*d*, ¹J_{P,Pt} = 2821 Hz), PPh₃]. Spectrum not previously reported. ¹H-NMR (CDCl₃, 300.13 MHz): δ 7.60–7.21 (30H, *m*, H-Ar), 4.39 [*s*, (*d*, ³J_{H,Pt} = 38.8 Hz), (*t*, ⁴J_{H,P} = 1.89 Hz), CCH₂C]. Lit. [11] δ 7.34 (*m*), 4.38 [*s*, (*d*, ³J_{H,Pt} = 38 Hz), (*t*, ⁴J_{H,P} = < 1.5 Hz)]. ¹³C-NMR (CDCl₃, 75.47

MHz): δ 134.8 (*m*, C-3'), 131.6 (*d*, C-4'), 128.6 (*m*, C-2'), 127.6 [*s*, (*d*, $^1J_{\text{P,C}} = 59.0$ Hz), C-1'], 120.1 [*s*, C(CN)₂], 48.2 (*t*, CCH₂C). C(CN)₂ not resolved. Spectrum not previously reported.

3.3. X-ray structure determination of $1 \cdot \text{CHCl}_3$

Colourless needles of $1 \cdot \text{CHCl}_3$ were obtained by slow evaporation of a 1:1 chloroform/dichloromethane solution at 4°C. Unit cell dimensions and intensity data were obtained on a Siemens CCD SMART diffractometer at the University of Auckland. A crystal of dimensions 0.50 × 0.14 × 0.08 mm was used for the study and a total of 18153 reflections (of which 4847 were unique) in the range $1.66 < \theta < 28.14^\circ$ were collected at 203(2) K, with monochromatic Mo-K_α X-rays ($\lambda = 0.71073$ Å). The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω . The crystal to detector distance was 5.0 cm. The data set was corrected empirically for absorption using SADABS [18] ($T_{\text{max.}, \text{min.}} = 0.67, 0.34$). Crystal data: C₁₇H₁₆N₅OAu · CHCl₃, $M_r = 622.68$, monoclinic, space group $P2_1/c$, $a = 8.1674(1)$, $b = 24.6053(1)$, $c = 10.9283(2)$ Å, $\beta = 100.76(1)^\circ$, $U = 2157.55(5)$ Å³, $D_{\text{calc.}} = 1.917$ g cm⁻³, $Z = 4$, $F(000) = 1192$, $\mu(\text{Mo-K}_\alpha) = 7.21$ mm⁻¹. The gold position was located by the Patterson methods option of SHELXS-96 [19], and all further non-hydrogen atoms were located routinely (SHELXL-96) [19]. In subsequent full-matrix least-squares refinements based on F^2 , all non-hydrogen atoms were assigned anisotropic temperature factors, and all hydrogen atom position determined by calculation. The refinement converged with $R_1 = 0.0427$ for 4139 data with $I \geq 2\sigma(I)$, 0.0512 for all data; $wR_2 = 0.1125$ [$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 1.1607P]$ where $P = (F_o^2 + 2F_c^2)/3$], and G-o-F = 1.015. The final difference map only showed significant peaks and troughs of electron density, +3.67 and -2.82 e Å⁻³, respectively, adjacent to the gold atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, or can be obtained from author W. Henderson on request.

Acknowledgements

We thank the University of Waikato, and the New Zealand Lottery Grants Board for financial support of this work, A.G. Oliver and C.E.F. Rickard (University of Auckland) for collection of the X-ray data set, and B.K. Nicholson for helpful discussions.

References

- [1] K.J. Ivin, *Olefin Metathesis*, Academic Press, New York, 1983.
- [2] R.H. Grubbs, *Prog. Inorg. Chem.* 24 (1971) 1.
- [3] P.W. Jennings, L.L. Johnson, *Chem. Rev.* 94 (1994) 2241.
- [4] S.D. Chappell, D.J. Cole-Hamilton, *Polyhedron* 11–12 (1982) 739.
- [5] R.J. Puddephatt, *Coord. Chem. Rev.* 33 (1980) 149.
- [6] J. Feldman, R.R. Schrock, *Prog. Inorg. Chem.* 39 (1991) 1.
- [7] C.F.H. Tipper, *J. Chem. Soc.* (1955) 2045.
- [8] J. Vicente, M.T. Chicote, M.D. Bermúdez, *J. Organomet. Chem.* 268 (1984) 191.
- [9] M.B. Dinger, W. Henderson, *J. Organomet. Chem.* 547 (1997) 243.
- [10] M.B. Dinger, W. Henderson, *J. Organomet. Chem.* 557 (1998) 231.
- [11] M. Lenarda, R. Ros, M. Graziani, U. Belluco, *J. Organomet. Chem.* 65 (1974) 407.
- [12] D.J. Yarrow, J.A. Ibers, M. Lenarda, M. Graziani, *J. Organomet. Chem.* 70 (1974) 133.
- [13] For selected references detailing the use of silver(I) oxide in metallacyclic synthesis, see the following, and references therein: (a) D.L. Davies, J. Fawcett, R. Krafczyk, D.R. Russell, K. Singh, *J. Chem. Soc. Dalton Trans.* (1998) 2349. (b) M.B. Dinger, W. Henderson, B.K. Nicholson, A.L. Wilkins, *J. Organomet. Chem.* 526 (1996) 303. (c) W. Henderson, B.K. Nicholson, *Polyhedron* 15 (1996) 4015. (d) J.A. Daldy, J. Fawcett, W. Henderson, R.D.W. Kemmitt, D.R. Russell, *J. Chem. Soc. Dalton Trans.* (1994) 3383. (e) A.D. Burrows, D.M.P. Mingos, A.J.P. White, D.J. Williams, *J. Chem. Soc. Dalton Trans.* (1996) 149; *ibid.* 3805. (f) S.L. James, D.M.P. Mingos, X. Xu, A.J.P. White, D.J. Williams, *J. Chem. Soc. Dalton Trans.* (1998) 1335.
- [14] T.G. Appleton, H.C. Clark, L.E. Manzer, *Coord. Chem. Rev.* 10 (1973) 335.
- [15] M.B. Dinger, W. Henderson, *J. Organomet. Chem.* 560 (1998) 233.
- [16] P.A. Bonnardel, R.V. Parish, *J. Organomet. Chem.* 551 (1996) 221.
- [17] J.X. McDermott, J.F. White, G.M. Whitesides, *J. Am. Chem. Soc.* 98 (1976) 6521.
- [18] R.H. Blessing, *Acta Crystallogr.* A51 (1995) 33.
- [19] G.M. Sheldrick, SHELX-97, Program for Solving and Refining X-Ray Crystal Structures, University of Göttingen, Germany, 1997.