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First functionalized diorganotin (IV) derivative containing the imidobis(diphenylselenophosphinate-Se,Se') ligand. The synthesis and X-ray crystal structures of Bu$_2$Sn[{N(SePPh$_2$)$_2$-Se,Se'}$_2$] and Ph$_2$ClSn[N(SePPh$_2$)$_2$-Se,Se'] · H$_2$O

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Abstract

Reaction of the appropriate R$_2$SnCl$_2$ with the potassium salt of the imidobis(diphenylselenophosphinate-Se,Se') ligand (1c) in 1:2 stoichiometry yields n-Bu$_2$Sn[{N(SePPh$_2$)$_2$-Se,Se'}$_2$] (2) and Ph$_2$ClSn[N(SePPh$_2$)$_2$-Se,Se'] · H$_2$O (3). The crystal and the molecular structures of both compounds were determined by X-ray diffractometry. The core geometry in compound 2 is a quasi perfect octahedron. Two selenide ligands are coordinated symmetrically to the tin atom forming a spiro-bicyclic NP$_2$Se$_2$SnSe$_2$P$_2$N system [Σ(Se–Sn–Se) = 360°]. Both organo substituents are in trans positions [(C'–Sn–C'A) = 180.0(1)°] and they are almost perpendicular to the SnSe$_4$ plane. In derivative 3 only one selenium-based ligand is coordinated asymmetrically to the tin atom and unexpectedly a chlorine atom remains attached to the metal center. The geometry around the tin atom corresponds to a distorted trigonal bipyramid with the Se(1) and Cl atoms at the axial positions. © 1997 Elsevier Science S.A.

Keywords: Diorganotin derivative; Imidobis ligand; Organotin compound

1. Introduction

Organotin compounds have attracted a great deal of attention owing to their wide range of applications such as biocides [1], as homogeneous catalysts in industry [2], and more recently as antitumour agents [3]. Some structural studies of organotin compounds containing ligands with hetero-donor atoms have been carried out in order to examine the effect that the presence of heteroatoms has on the structure adopted by these compounds [2–6].

Recently, some of us reported the structure of both bis(imidotetraphenyldiselenodiphosphino-Se,Se')tin(II) isomers. The yellow isomer was found to exhibit a very unusual square-planar geometry around the tin atom [7]. This interesting behavior, as well as the successful single crystal X-ray studies of some organometallic derivatives containing non-rigid 'imidodiphosphinate' ligands (1) [1] with sulfur (1b [5,6]) and oxygen (1a [8]) as donor atoms, prompted us to synthesize the organometallic derivatives containing the analogous selenium-based ligands (1c). Thus allowing the comparison of the selenium versus sulfur and oxygen atoms as the donor set.

1a X = O

1b X = S

1c X = Se

We wish to report here two new organotin derivatives, namely n-Bu$_2$Sn[{N(SePPh$_2$)$_2$-Se,Se'}$_2$] (2) and a

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[1] Chem. Abs. entry under N-(diphenylphosphinooyl)-P, P-diphenylphosphinimidic acid (1a), N-(diphenylphosphinothioyl)-P, P-diphenylphosphinothioic amide (1b), and N-(diphenylphosphinoselenoyl)-P, P-diphenylphosphinoselenoic amide (1c).

partially substituted compound $Ph_2ClSn[N(SePPh_2)_2$-
Se,Se'] · H_2O (3), corresponding to the first example of
a functionalized imidobis(diphenylselenophosphinate-
Se,Se')diorganotin(IV) derivative. Both compounds have
been characterized by microanalysis, multielement
NMR, IR, positive ion FAB mass spectroscopy, and by
single crystal X-ray diffraction.

2. Description of the structures

The structures consist of discrete
$[R_2Sn\{(SePPh_2)_2N\}_nCl_{2-n}]$ molecules (2: $n = 2$; R =
n-Bu; 3: $n = 1$; R = Ph), there being no significant
intermolecular contacts in the crystal lattice. The molec-
ular structure and atomic labeling scheme of
$[Bu_2Sn\{(SePPh_2)_2N\}_2]$ (2) is illustrated in the ORTEP
plot of Fig. 1. The structure of the compound 3, which
was found to crystallize as the $Ph_2ClSn[N(SePPh_2)_2$-
Se,Se'] · H_2O solvate, is shown in Fig. 2. Selected bond
distances and angles are listed in Table 1. Both organ-
otin derivatives exhibit a very different geometry around
the tin atom.

Two selenide ligands are symmetrically coordinated
to the tin atom forming two inorganic $SnSe_2P_2N$ metal-
locycles (av. Sn–Se 2.844(3) Å). This contrasts with the
notable asymmetrical coordination mode displayed by
the ligand in the square-planar $[Sn\{(SePPh_2)_2N$-
Se,Se')$_2$] complex and in its pyramidal isomer [7]. The
$SnSe_4$ system is coplanar [$\Sigma(Se–Sn–Se) = 360°$] with
trans Se–Sn–Se bond angles of 180.0(1)°. The endo-
cyclic Se–Sn–Se angles (Se(1)–Sn–Se(2) 90.3(1)°) are
only a little larger than the exocyclic ones (Se(1)–Sn–
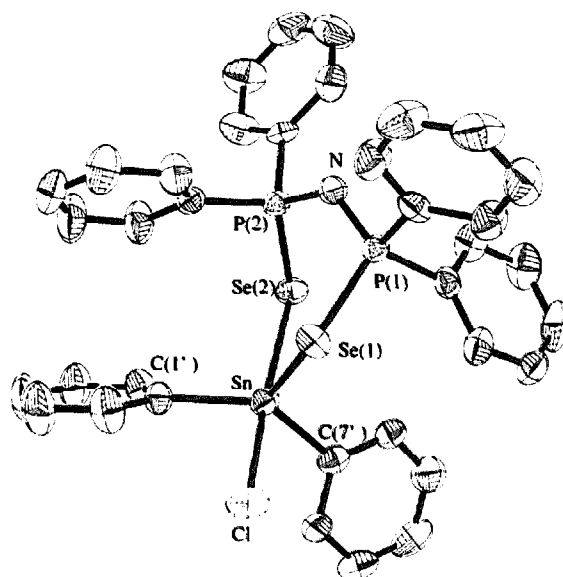
Fig. 2. ORTEP plot of $Ph_2ClSn[N(SePPh_2)_2$-*Se.Se'*]·H_2O (3), with
thermal ellipsoids at the 50% probability level. Hydrogen atoms are
omitted for clarity.

Se(2A) 89.7(1)°) (Δ(endo–exo) = 0.6°). As observed
for R_2SnCh_2 (Ch = bidentate ligand) structures contain-
ing ligands with large bite [9], in compound 2 both
organo substituents are *trans* (av. Sn–C(1') 2.169(9) Å)
with a C(1')–Sn–(Cl'A) angle of 180.0(1)°. They are
almost perpendicular to the $SnSe_4$ plane (Table 2), thus
leading to a quasi perfect *trans*-octahedral geometry
around the central atom.

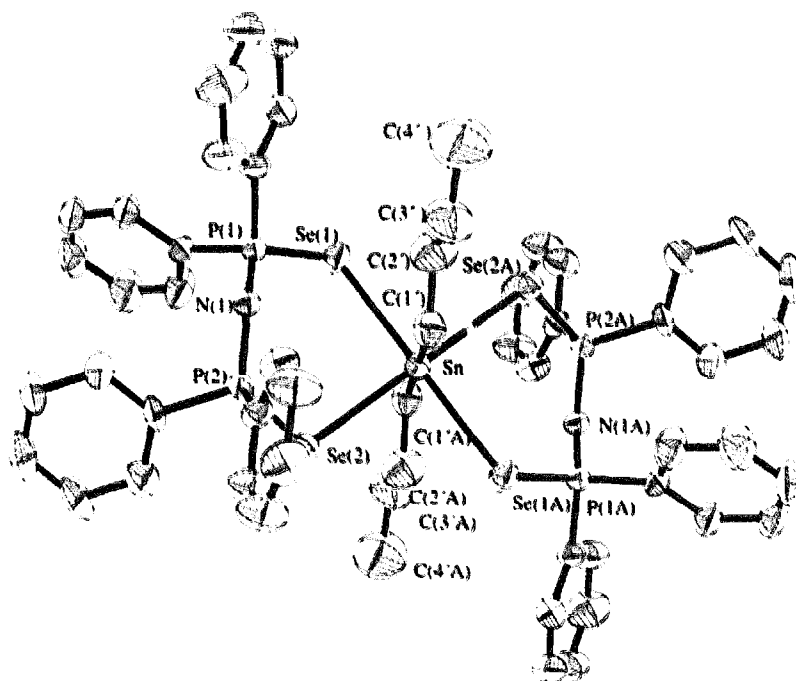A very similar structure was also observed in two of

Fig. 1. ORTEP plot of *n*-$Bu_2Sn[\{N(SePPh_2)_2$-*Se.Se'*$\}_2]$ (2), with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

the diorganotin derivatives with the analogous sulfur- and oxygen-based ligands [R$_2$Sn{(XPPh$_2$)$_2$N}$_2$] (R = Me, X = S [5] and R = n-Bu, X = O [8]). However, the difference between endo and exocyclic X–Sn–X (X = O, S, Se) angles is markedly larger in the case of the thio dimethyl derivative (Δ(endo–exo) = 15.6°) [5], while it is reversed in the oxo di-n-butyl analogue (Δ(exo–endo) = 3.0°) [8] and in the tin(II) square-planar complex [7] (Δ(exo–endo) = 4.0–3.2°).

The SnSe$_2$P$_2$N chelate rings are arranged in a distorted boat conformation with the metal and nitrogen atoms at the apices, as is observed in the tin(II) pyramidal isomer [7] and in most of the structures of the derivatives involving the ligands 1a and 1b [10,11]. The average P–N (av. 1.597(7) Å) and P–Se bond lengths (av. 2.166(3) Å) are consistent with a π-delocalized structure involving the five ligand atoms in the chelate ring, as has been noted in cyclic phosphazenes [12].

In contrast, in the diphenyltin derivative 3 only one selenium-based ligand is coordinated to the tin atom and unexpectedly a chlorine atom is still attached to the metal center. The resulting geometry around the tin atom is best described as a distorted trigonal bipyramid. The Se(1)–Sn–Cl angle (174.0(1)°) corresponds to the diaxial angle, while the equatorial angles (av.

Table 1
Selected bond lengths (Å) and angles (°) for 2, and 3·H$_2$O

	2	3
Sn–Se(1)	2.843(1)	2.603(1)
Sn–Se(2)	2.847(1)	2.868(1)
Sn–C(1') [a]	2.167(9)	2.133(9)
Sn–C(7')		2.154(8)
Sn–Cl		2.519(3)
N–P(1)	1.593(6)	1.582(7)
N=P(2)	1.596(6)	1.611(7)
P(1)–Se(1)	2.167(2)	2.214(2)
P(2)–Se(2)	2.165(2)	2.170(2)
Se(1)–Sn–Se(2)	90.3(1)	95.7(1)
Se(1)–Sn–Se(2A)	89.7(1)	
Se(1)–Sn–Se(1A)	180(1)	
Se(1)–Sn–Cl		78.5(1)
Se(2)–Sn–Cl		174.0(1)
Se(1)–Sn–C(1')	84.9(3)	119.0(2)
Se(2)–Sn–C(1')	85.8(2)	88.4(2)
Se(1)–Sn–C(1'A)	95.1(3)	
Se(2)–Sn–C(1'A)	94.2(2)	
C(1')–Sn–C(1'A)	180.0(1)	
Se(1)–Sn–C(7')		119.1(2)
Se(2)–Sn–C(7')		92.3(2)
Cl–Sn–C(1')		93.2(2)
Cl–Sn–C(7')		91.8
C(1')–Sn–C(7')		121.5(3)
P(1)–N(1)–P(2)	134.3(5)	126.2(4)
Sn–Se(1)–P(1)	104.2(1)	102.2(1)
Sn–Se(2)–P(2)	106.6(1)	106.8(1)
N(1)–P(1)–Se(1)	119.3(3)	117.2(3)
N(1)–P(2)–Se(2)	119.5(2)	116.5(3)

[a] Primed atoms generated by 1̄ symmetry.

Table 2
Crystallographic data for 2, and 3

Compound	2	3
Formula	C$_{56}$H$_{58}$N$_2$P$_4$Se$_4$Sn	C$_{36}$H$_{30}$NP$_2$ClSe$_2$Sn.H$_2$O
Formula mass	1317.5	868.6
Color, habit	Light yellow, prism	Colorless, prism
Crystal size (mm)	0.4×0.34×0.26	0.4×0.26×0.08
F(000)	1308	1712
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$/n	P2$_1$/c
a [Å]	9.211(1)	9.675(1)
b [Å]	15.391(1)	21.763(3)
c [Å]	19.817(1)	16.965(1)
β [°]	97.98(1)	92.34(1)
V [Å^3]	2783.2(4)	3568.9(7)
Z	2 [a]	4
ρ_{calcd} [mg/cm^3]	1.572	1.617
μ [mm^{-1}]	3.227	2.949
Min./max.	0.4832/0.5818	0.4729/0.7943
Transmission	0.70/−0.60	0.88/−0.55
Max./min. peaks in final diff. map (eÅ^{-3})		
R, R_w (F_0)% [b]	5.44, 5.84 [c]	4.68, 5.09 [d]
Goodness-of-fit	1.04	1.02

[a] Compound with crystallographic C_i symmetry; Sn atom at ($\frac{1}{2}$, 0, 0).

[b] $R = \Sigma \|F_o - F_c\|/\Sigma |F_o|$, $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

[c] The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0010F^2$.

[d] The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0008F^2$.

119.8(1.4)°) are those between the Se(2) atom and both carbon atoms from the phenyl groups [C(1') and C(7')]. Only one of the remaining equatorial bond angles at the tin atom varies notably from the ideal value of 90° (Se(2)–Sn–Cl angle = 78.5(1)°). The axial Sn–Cl bond length is 5.4% larger than the covalent radii sum [13]. The selenide ligand displays an asymmetrical coordination, resulting in a substantially increased bonding between the metal center and the axial Se(1) atom (Δ = 0.26 Å). The remaining P–Se and P–N bonds also follow an alternating pattern, which is consistent with some localization of the bonding along the metallocycle (Table 1). This behavior was noted before in some structures of the tin(II) and lead(II) bis-chelates [7,14] and of the Bi(III) and Sb(III) tri-chelates [10] with the selenide ligand 1c. The MSe$_2$P$_2$N chelate ring exhibits also a distorted boat conformation, but the P(1) and the Se(2) atoms lie at the apices, as in many of the structures involving this ligand [10].

Comparison with the structure of the free ligand 1c [15] reveals that the P–Se bond lengths in these derivatives are considerably increased [1c, av. P–Se 2.092(8) Å], whilst the P–N bond distances are shortened [1c, av. P–N 1.682(4) Å] (Table 2). This has also been noted in previous analogous structures [11] as a consequence of deprotonation and coordination. The N–P–Se angles are

notably enhanced in **2** [**1c**, av. Se–P–N 115.4(9)°], but only marginal increased in **3**. The P–N–P angles are increased in the octahedral derivative **2** [**1c**, av. P–N–P 122.2(2)°], but they are contracted in the distorted trigonal bipyramidal compounds **3** (Table 1).

3. Experimental

3.1. General and instrumental

Diorganotin chlorides [R_2SnCl_2 (R = n-Bu, Ph)] and solvents were commercial products and were used without further purification. The imidobis(diphenyl-selenophosphinate-Se,Se') ligand (**1c**), was synthesized and converted to its potassium salt (KL) according to the method of Woollins et al. [15]. The FAB mass spectra were measured on a 3-nitrobenzyl alcohol support in the positive ion mode on a Jeol JMS-SX102A instrument and the infrared spectra (as KBr discs) on a Perkin Elmer 283B spectrometer. The ^{1}H-(500 MHz) and ^{13}C-(125 MHz) NMR spectra were recorded in $CDCl_3$ on a Varian Unity Plus 500 spectrometer (external reference: TMS), while the ^{31}P-(121 MHz), ^{77}Se-(51.2 MHz) and ^{119}Sn-(111.8 MHz) NMR spectra were recorded in $CDCl_3$ for **2** and CD_2Cl_2 for **3** on a Varian VXR 300s spectrometer using as external reference H_3PO_4 85%, Ph_2Se and $Sn(CH_3)_4$, respectively. Chemical shifts are reported in ppm and coupling constants in Hertz. Microanalyses were performed by Galbraith Laboratories.

3.2. Synthesis of n-$Bu_2Sn[N(SePPh_2)_2$-$Se,Se']$ (2)

A solution of n-Bu_2SnCl_2 (0.075g, 0.247 mmol) in 10 cm³ of methanol was added to an methanolic solution of KL (0.301g, 0.518 mol) in 50 cm³ of methanol, with stirring. The precipitated light yellow solid was filtered, washed with methanol and dried in vacuo. Yield 0.2802 g (86.11%), m.p. 205–6°C. Anal. Found: C, 51.2; H, 4.3 Calc for $C_{36}H_{38}N_2P_2Se_4Sn$:C, 51.05; H, 4.43%. IR (cm⁻¹) 1234 s, br [ν(P–N)] +1176 s [ν(P–N)/δ(CH)]; 743 m [ν(P–N)]; 532 s [γ(PNP)/ν(P–Se)]. MS (FAB⁺, CH_3Cl, for ^{80}Se) (m/z): 1260 [$BuSe_4(PPh_2)_4N_2Sn^+$], 662 [$Se_2(PPh_2)_2NSn^+$], 544 [$Se_2(PPh_2)_2N^+$], 464 [$Se(PPh_2)_2N^+$], ^{31}P NMR δ = 28.287s, ^{77}Se NMR δ = –50.76d ($^1J(^{31}P$–$^{77}Se) = 584.4$), ^{119}Sn NMR δ = –195.943s.

3.3. Synthesis of $Ph_3ClSn[N(SePPh_2)_2$-$Se,Se']\cdot H_2O$ (3)

A solution of Ph_3SnCl_2 (0.085 g, 0.25 mmol) in 10 ml of methanol was added to an methanolic solution of

KL (0.303 g, 0.52 mmol) in 50 ml of methanol. The white solid precipitated was filtered, washed with water and methanol, and dried in vacuo. Yield 0.1876 g, (86.4%), m.p. 197–198°C. Anal. Found: C, 50.72%; H, 3.45%. Calc. for $C_{36}H_{30}NP_2Se_2ClSN$: C, 50.83; H, 3.55%. IR (cm⁻¹) 1188 s, br [ν(P–N)] +1171 s [ν(P–N)/δ(CH)]; 543 s [γ(PNP)/ν(P–Se)]. MS (FAB⁺, CH_3Cl, for ^{80}Se) (m/z): 816 [$Ph_2Se_2(PPh_2)_2NSn^+$], 774 [$PhClSe_2(PPh_2)_2NSn^+$], 662 [$Se_2(PPh_2)_2NSn^+$], 544 [$Se_2(PPh_2)_2N^+$], 464 [$Se(PPh_2)_2N^+$], 384 [$(PPh_2)_4N^+$]. ^{31}P NMR δ = 31.875t ($^1J(^{31}P$–$^{77}Se) = 511.8$). ^{119}Sn NMR δ = –289t ($^2J(^{119}Sn$–$^{31}P) = 64.1$).

We attempted unsuccessfully to synthesize other compounds such as $Me_3Sn[SeP(Ph)_2NP(Ph)_2Se]$, $Me_2Sn[SeP(Ph)_2NP(Ph)_2Se]_2$, t-$Bu_2Sn[SeP(Ph)_2NP(Ph)_2Se]_2$ and $Ph_3Sn[SeP(Ph)_2NP(Ph)_2Se]$, using several different solvents, and also starting from the free ligand or from the hydroxo and chloro organotin compounds.

3.4. X-ray diffraction studies

Crystals suitable for X-ray analysis were obtained by slow diffusion of n-hexane into chloroform solutions for **2** and n-hexane–dichloromethane solutions for **3**. Data collection was performed at room temperature on a Siemens P4 four-cycle diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å), using the ω–2θ scan technique. A total of 8568 (3° < 2θ < 60°) for **2** and 6621 (3° < 2θ < 50°) reflections for **3** was measured, from which 3743 (**2**) and 3931 [$F > 4.0\sigma(F)$] (**3**) were used for calculations. In both cases, data were corrected for background and Lorentz–polarization effects and also an absorption correction (face-indexed numerical method) was applied. Crystallographic data are summarized in Table 2. The structures were solved by direct methods using the Siemens SHELXTL-PLUS program (PC version) [16] and refined by full-matrix least-square calculations. The numbers of refined parameters were 305 for **2** and 404 for **3**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated as a riding model with fixed isotropic U = 0.06. Lists of additional data, including atom coordinates and anisotropic temperature factors have been deposited as supplementary material.

Acknowledgements

References

[1] See, for example: S.J. Blunden, A. Chapman, in P.J. Craig (Ed.), Organometallic Compounds in the Environment, Longman, Harlow, 1986; and refs. therein.

[2] (a) C.S. Parulekar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins, E.R.T. Tiekink, J. Organomet. Chem. 372 (1989) 193; (b) C.S. Parulekar, V.K. Jain, T. Kesavadas, E.R.T. Tiekink, J. Organomet. Chem. 387 (1990) 163; and refs. therein.

[3] (a) E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1; (b) I. Haiduc, C. Silvestru, Coord. Chem Rev. 99 (1990) 253.

[4] C. Silvestru, I. Haiduc, J. Organomet. Chem. 365 (1989) 83; and refs. therein.

[5] I. Haiduc, C. Silvestru, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Polyhedron 12 (1993) 69.

[6] (a) R. Roesler, C. Silvestru, I. Haiduc, F. Kayser, M. Gielen, B. Mahieu, Main Group Met. Chem. 16 (1993) 435; (b) K.C. Molloy, C. Silvestru, M. Mahon, I. Haiduc, Polyhedron 14 (1995) 1169.

[7] R. Cea-Olivares, V. García-Montalvo, J. Novosad, J D. Woollins, A.M.Z. Slawin, G. Espinosa-Pérez, P. García y García, J. Chem. Soc. Chem. Commun. (1996) 519.

[8] C. Silvestru, I. Haiduc, R. Cea-Olivares, A. Zimbron, Polyhedron 13 (1994) 3159.

[9] (a) W.F. Howard, R.W. Crecely, W.H. Nelson, Inorg. Chem. 24 (1985) 2204; (b) V.S. Petrosyan, Prog. Nucl. Magm. Reson. Spectrosc. 11 (1977) 115.

[10] R. Cea-Olivares, V. García-Montalvo, J. Novosad, J.D. Woollins R.A. Toscano, G. Espinosa-Pérez, Chem. Ber. 35 (1996) 3948.

[11] (a) V. García-Montalvo, R. Cea-Olivares, D.J. Williams, G. Espinosa-Pérez, Inorg. Chem. 35 (1996) 3948; (b) J.S. Casas, I. Haiduc, A. Sánchez, J. Sordo, E.M. Vázquez-López, Polyhedron 13 (1994) 2873; and refs therein.

[12] H.R. Allcock, Phosphorus–Nitrogen Compounds, Academic Press, New York, 1972.

[13] J.E. Huheey, Inorganic Chemistry, 3rd ed., Harper, New York, 1983.

[14] V. García-Montalvo, J. Novosad, P. Kilian, J.D. Woolins, A.M.Z. Slawin, P. García y García, M. López-Cardoso, G. Espinosa-Pérez, R. Cea-Olivares, J. Chem. Soc. Dalton Trans., (1997) 1025.

[15] P. Bhattacharyyaa, J. Novosad, J.J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1995) 1607

[16] SHELXTL PLUS, version 4.0, Siemens Analytical Instruments, Madison, WI, 1989; SHELXTL PC, version 4.1, Siemens Analytical Instruments, Madison, WI, 1990.