Macrobicyclic Titanium(IV) Complexes with C_3-Symmetric Synthetic Peptides**

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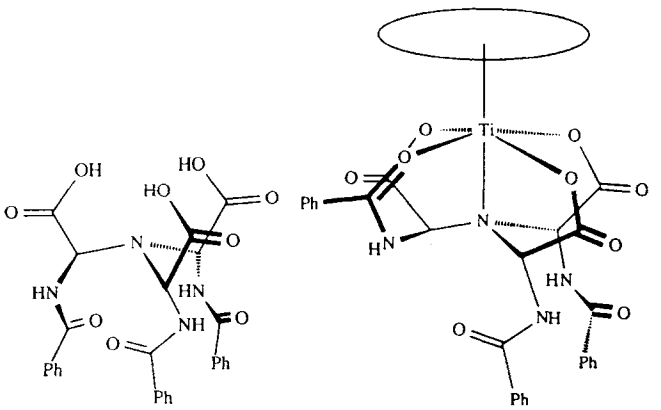
Dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday

The synthesis of C_3-symmetric pseudo-peptides[1] has been achieved during studies related to the chemistry of electrophilic glycine equivalents. The tricarboxylic acid 2,2′,2″-nitrilotris-[2-(benzoylamino)acetic acid], N(BzGly*OH)$_3$ **1** is accessible in a few further steps from the coupling of methyl α-bromohippurate with ammonia. This compound, which is stabilized by three intramolecular hydrogen bonds, has proven to be a suitable template for the synthesis of C_3-symmetric pseudo-peptides with defined geometry.[1] The coordination properties of this class of compound are of interest for several reasons. Firstly, applications as chiral ligands for stereoselective synthesis seem possible;[2] and secondly, peptides with a well-defined metal coordination site are model compounds for metalloenzymes.[3] The reaction of $[(\eta^5\text{-}C_5H_5)TiCl_3]$ or $[(\eta^5\text{-}C_5Me_5)TiCl_3]$[4] with the trianion of **1** (*RRR*/*SSS*) yields the complexes **2** and **3**. The



1
RRR/SSS

$[(\eta^5\text{-}C_5H_5)Ti(1)]$ **2**

$[(\eta^5\text{-}C_5Me_5)Ti(1)]$ **3**

X-ray structural analysis[5] of **3** (Fig. 1) shows the pseudo-amino acid functions as a pentadentate ligand: besides the titanatrane-like complexation,[6] coordination of a benzoyl O atom occurs.

If the Cp* ring is regarded as an unidentate ligand, the environment around the titanium atom can be described as distorted octahedral. The Ti atom resides slightly above the plane formed from the O atoms O1, O3, O4, and O7. The molecular structure also provides an explanation for the remarkable stability[7] of the complexes **2** and **3**: the ligand causes the complete sterical shielding of the Ti atom.

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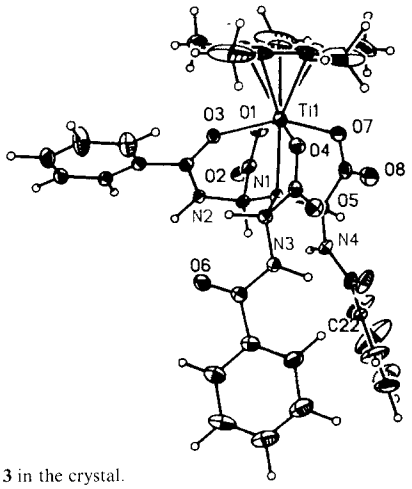

Fig. 1. Molecular structure of **3** in the crystal.

An important aspect of the structure of **3** is the stabilization by inter- and intramolecular hydrogen bonds. By coordination of the benzoyl group two of—in the free ligand three—intramolecular hydrogen bonds between the amide-N and -O atoms are broken. The amide N atoms N2 and N4 "released" by this coordination now form intermolecular hydrogen bonds: N2–H to a water molecule present in the crystal (not shown in Fig. 1), N4–H to the carboxylate-O atom of an adjacent molecule. This leads to a dimerization of the complex in the crystal (Fig. 2). Interestingly both enantiomers (*RRR* and *SSS*) are linked through hydrogen bonds.[8]

This structural type is consistent with the spectroscopic data also for **2**. The lowering of the ligand symmetry is manifested in the NMR spectra. They show separate signals for the three hippuric acid residues. The ^{1}H NMR signals of the amino acid ligand of **3** in [D$_6$]DMSO are substantially broadened at elevated temperatures. This coalescence phenomenon is presumably a consequence of an exchange between coordinated and free benzoyl groups. Treatment of the disodium salt of **1** with $[(\eta^5\text{-}C_5H_5)TiCl_2]$ in methanol also affords **2** as the major product (NMR-spectroscopic proof). Presumably a double substitution of carboxylato for chloro ligands occurs first, followed by an

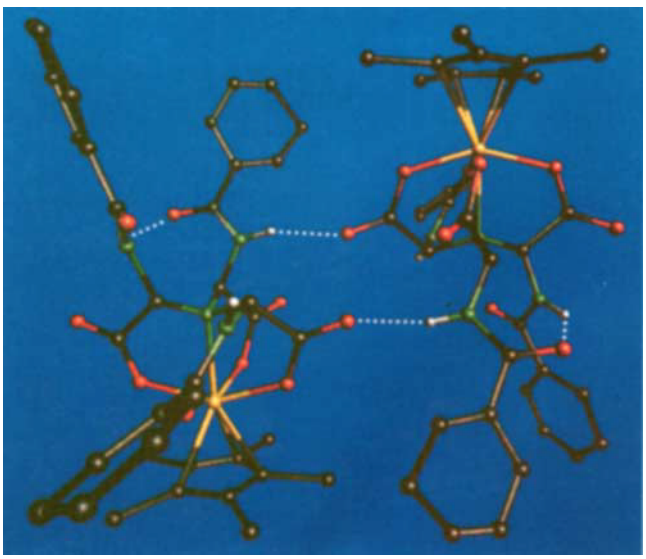

Fig. 2. Dimerization of **3** through hydrogen bonds.

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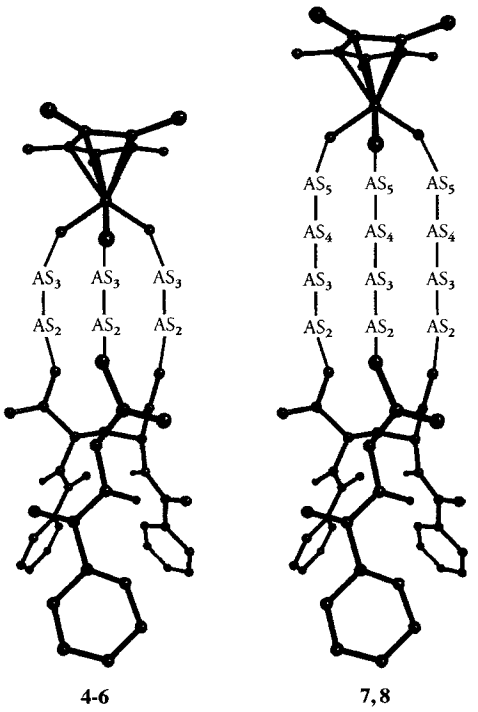
intramolecular protolysis of a cyclopentadienyl ligand by the remaining acid function.

Pseudo-peptides, prepared starting from **1**, exhibit a uniform basic structure stabilized by hydrogen bonds in the crystalline state.[11] Hence they should be ideally preorganized for the formation of macrobicycles. Amino acids with sterically demanding side chains were chosen deliberately for the C-terminii; these shield the titanium atom, and consequently stabilize the complexes and prevent a di- or oligomerization through intermolecular coordination of the metal atom.

The reaction of the pseudo-nonapeptides N(BzGly*GlyLeuOH)$_3$, N(BzGly*GlyPheOH)$_3$, and N(BzGly*LeuPheOH)$_3$ with three equivalents of sodium methoxide in dichloromethane and subsequent treatment with [Cp*TiCl$_3$] gives the complexes **4**–**6**, respectively (depicted schematically in Fig. 3). These complexes can be isolated by extraction with dichloromethane/ether (**4** and **5**) or dichloromethane/pentane (**6**). In this way, side products can be separated quantitatively. The yields of the reactions are above 50%. The pseudo-nonapeptides used for the synthesis of compounds **4** and **6** were purified by fractional crystallization before saponification. One of the two diastereoisomers is thereby separated. The absolute configuration of the ligands in these compounds (*RRR* in **4**; *SSS* in **6**) can be determined by recording the CD spectra.[11] A mixture of isomers (ca. 2.5:1) was used for the synthesis of **5**. During complexation and/or the subsequent workup procedures for **5** one diastereomer (*SSS*) becomes enriched (ca. 5:1).



4-6 **7,8**

	AS$_2$	AS$_3$	AS$_4$	AS$_5$
4	Gly	Leu		
5	Gly	Phe		
6	Leu	Phe		
7	Val	Val	Gly	Val
8	Val	Leu	Gly	Phe

Fig. 3. Schematic representation of the macrobicyclic Cp*Ti^{IV} complexes **4**–**8** (AS = α-amino acid).

To record the NMR spectra of compounds **4**–**6**, low concentrations of the samples are required (below 0.8 mM), since at higher concentrations, considerable line broadening is observed, presumably due to aggregation. The spectra show one set of signals for the three peptide chains in each case. This proves that in solution the C_3 symmetry of the peptide ligands remains intact after complexation. An exact assignment of the ^{1}H NMR signals was achieved with the help of H-H-COSY spectra. The shifts of the amide protons of AS$_1$ and AS$_2$ indicate the presence of six intramolecular hydrogen bonds in **4**–**6**, similar to the situation in the uncomplexed pseudo-peptides. Only the amide protons of the C-terminal amino acids (AS$_3$) apparently do not form hydrogen bonds. The "Cp*Ti-lid" provides additional rigidity for the peptide frame. This becomes noticeable in the ^{1}H NMR spectra by the difference between the chemical shifts of diastereotopic protons.[9] Thus, the signals of the glycine methylene protons (AS$_2$) in the free ligand are separated by 0.6 ppm, those in **5** by 1.1 ppm. This effect is less marked for the diastereotopic methylene protons of the phenylalanine or leucine side chains.

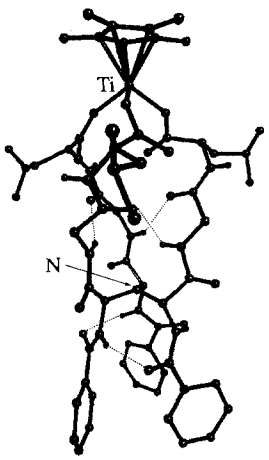


Fig. 4. Simulation of the molecular structure of **4**.

Figure 4 shows a simulation of the molecular structure of **4**.[10] This was performed on the basis of structural data of N(BzGly*GlyLeuOMe)$_3$.[11] The basic framework fixed by hydrogen bonds was used unchanged, the carboxylate groups of the leucine residues were rotated (without change of symmetry) into a position favorable for complexation, and the methyl ester functions replaced by the Cp*Ti fragment. The lipophilic leucine side chains point away from the molecular axis and are an important reason for the good solubility of **4** in organic solvents. The same holds for the phenylalanine and leucine side chains of compounds **5** and **6**. As the three peptide chains are bound relatively close to each other through hydrogen bonds, the space inside the molecules appears too small for a hypothetical guest molecule.

In Figures 3 and 4, the carboxylate groups are shown as unidentate ligands; however, an η^2-coordination with formation of four-membered chelate rings cannot be ruled out either on the basis of NMR or IR spectroscopic data. This holds for compounds **4**–**6** as well as for the following compounds **7** and **8**.

In order to explore the limitations of this synthetic concept, two pseudo-pentadecapeptides, [N(BzGly*ValValGlyValOMe)$_3$ and N(BzGly*ValLeuGlyPheOMe)$_3$], were prepared. Also here amino acids with lipophilic side chains were chosen deliberately to increase the solubility. The synthesis of the macrobicyclic complexes **7** and **8** (ring size 32 atoms) was achieved analogously to that for **4**–**6**; however as expected the yields are lower (13% for **7**; 6% for **8**), the solubility in dichloromethane likewise. The molecular structures of **7** and **8** are shown schematically in Figure 3.

The cyclopentadienyl–Ti^{IV} complexes presented here are examples for the use of C_3-symmetric peptide bundles as ligands. We are currently investigating whether by suitable functionalization of the peptide chains it is possible to introduce other metal fragments into the peptide bundles.

Experimental Procedure

The pseudo-amino acid and peptide esters used were prepared as described in ref. [1], and subsequently saponified with LiOH in THF/water. The synthesis of complexes **2**–**8** was performed under argon with dry purified solvents. FAB mass

spectra were obtained for all complexes. The isotopic distribution corresponded to the calculated values within the precision limits of the experiment. All compounds gave satisfactory elemental analyses.

2: A solution of **1** (219 mg, 0.40 mmol) in methanol (10 mL) was treated with a methanolic NaOMe solution (1.20 mmol) and stirred for 45 min at room temperature. After addition of [CpTiCl$_3$] (86 mg, 0.39 mmol) and 2.5 h stirring, a yellow precipitate formed from the originally clear solution. The suspension was concentrated in vacuo to 5 mL and stirred for 30 min at 0 °C. The precipitate was isolated by centrifugation and recrystallized from dichloromethane/hexane. Yellow crystals were obtained by layering an ethyl acetate solution with hexane. Yield 176 mg (66%), m.p. >175 °C (decomp).-IR (KBr): $\tilde{\nu}$ = 1673 cm^{-1} vs and br. (CO$_2$ and CON), 1602 s, 1563 s and 1525 s (CON). – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.87 (d, ^3J = 6 Hz, 1H, NHCH), 5.28 (d, ^3J = 7 Hz, 1H, NHCH), 5.79 (d, ^3J = 9 Hz, 1H, NHCH), 6.94 (s, 5H, Cp), 7.23–7.63 (m, 11H, Ph), 7.74 (d, ^2J = 9 Hz, 1H, NHCH), 7.78 (dd, ^3J = 7, ^4J = 1 Hz, 2H, *o*-Ph), 7.95 (d, ^3J = 7 Hz, 1H, NHCH), 7.99 (dd, ^3J = 8, ^4J = 1 Hz, 2H, *o*-Ph), 9.38 (d, ^3J = 6 Hz, 1H, NHCH). – ^{13}C NMR (100.5 MHz, CDCl$_3$): δ = 66.24, 69.63 and 77.81 (NHCH), 127.84, 127.88, 128.16, 128.43, 128.61, 129.91, 131.85, 132.05, 132.68, 132.73 and 135.65 (Cp and Ph), 168.24, 169.27, 169.49, 169.73, 170.55 and 170.70 (CO$_2$ and CON).

3: Synthesis analogous to that for **2** in methanol (20 h, room temperature). Purification by extraction with dichloromethane and recrystallization from ethyl acetate/hexane. Red crystals, yield 198 mg (68%), m.p. >197 °C (decomp).-IR (Nujol): $\tilde{\nu}$ = 1714 cm^{-1} s (CON, coord.), 1670 s and 1647 s (CO$_2$ and CON), 1597 s, 1560 s and 1525 s (CON). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.21 (s, 15H, Cp*), 4.79 (d, ^3J = 7 Hz, 1H, NHCH), 5.11 (d, ^3J = 7 Hz, 1H, NHCH), 5.64 (d, ^3J = 9 Hz, 1H, NHCH), 6.82 (d, ^3J = 9 Hz, 1H, NHCH), 7.22–7.62 (m, 11H, Ph), 7.73 (dd, ^3J = 8, ^4J = 1 Hz, 2H, *o*-Ph), 7.83 (d, ^3J = 7 Hz, 1H, NHCH), 7.95 (dd, ^3J = 8, ^4J = 1 Hz, 2H, *o*-Ph), 8.77 (d, ^3J = 7 Hz, 1H, NHCH). – ^{13}C NMR (100.5 MHz, CD$_3$OD): δ = 13.01 [C$_5$(CH$_3$)$_5$], 67.05, 67.96 and 71.03 (NHCH), 128.63, 129.05, 129.10, 129.38, 129.50, 129.70, 130.46, 132.90, 133.22, 133.45, 134.11, 135.61 and 137.86 [C_5(CH$_3$)$_5$ and Ph], 170.56, 171.25, 172.50, 172.70, 173.50 and 173.91 (CO$_2$ and CON).

4: A solution of N(BzGly*GlyLeuOH)$_3$ (159 mg, 0.15 mmol) in dichloromethane (20 mL) was treated with a methanolic NaOMe solution (0.41 mmol) and stirred for 2 h at room temperature. Then a solution of [Cp*TiCl$_3$] (39 mg, 0.14 mmol) in dichloromethane (5 mL) was added slowly, the solution stirred for another 2 h and the solvent was evaporated in vacuo. The residue was extracted with a 1:1 mixture of dichloromethane and ether (15 mL). The resulting solution was concentrated in vacuo to about 1 mL. The product precipitated after addition of pentane (20 mL) and was washed with pentane (20 mL). Orange powder. Yield 104 mg (56%), m.p. >196 °C (decomp).-IR (KBr): IR (KBr): $\tilde{\nu}$ = 1659 cm^{-1} vs (CO$_2$ and CON), 1525 vs (CON). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.95 [d, ^3J = 6 Hz, 9H, CH(CH_3)$_2$], 1.00 [d, ^3J = 7 Hz, 9H, CH(CH_3)$_2$], 1.43–1.78 [m, 9H, CH(CH$_3$)$_2$ and CH$_2$-Leu], 2.12 (s, 15H, Cp*), 3.54 (dd, ^2J = 16, ^3J = 3 Hz, 3H, CH$_2$-Gly), 4.50 (dt, ^3J = 10, $^3J'$ = 10, $^3J''$ = 5 Hz, 3H, NHCH-Leu), 4.68 (dd, ^2J = 16, ^3J = 9 Hz, 3H, CH$_2$-Gly), 5.65 (d, ^3J = 10 Hz, 3H, NH-Leu), 5.84 (d, ^3J = 10 Hz, 3H, NHCHN), 7.11 (t, ^3J = 8 Hz, 6H, *m*-Ph), 7.29 (t, ^3J = 8 Hz, 3H, *p*-Ph), 7.37 (d, ^3J = 8 Hz, 6H, *o*-Ph), 8.61 (d, ^3J = 10 Hz, 3H, NHCHN), 8.70 (m, 3H, NHCH$_2$). – ^{13}C NMR (100.5 MHz, CDCl$_3$): δ = 12.05 [C$_5$(CH_3)$_5$], 21.72, 23.16 and 24.72 [CH(CH_3)$_2$ and CH(CH_3)$_2$], 40.27, 42.50, 51.39 (CH$_2$-Leu, NHCH-Leu and CH$_2$-Gly), 62.85 (NHCHN), 127.47, 127.90, 131.13, 133.53 and 135.15 [C_5(CH$_3$)$_5$ and Ph], 166.94, 168.51 and 169.93 (CO$_2$ and CON).

5: Synthesis analogous to that for **4**; extraction with dichloromethane/ether (2:3) (20 mL). Orange powder. Yield 128 mg (53%), m.p. >194 °C (decomp).-IR (KBr): $\tilde{\nu}$ = 1658 cm^{-1} vs (CO$_2$ and CON), 1524 vs (CON). – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.04 (s, 15H, Cp*), 2.80 (dd, ^2J = 15, ^3J = 10 Hz, 3H, CH$_2$-Phe), 3.14 (dd, ^2J = 15, ^3J = 5 Hz, 3H, CH$_2$-Phe), 3.33 (dd, ^2J = 16, ^3J = 4 Hz, 3H, CH$_2$-Gly), 4.41 (dd, ^2J = 16, ^3J = 10 Hz, 3H, CH$_2$-Gly), 4.66 (m, 3H, NHCH-Phe), 5.57 (d, ^3J = 9 Hz, 3H, NH-Phe), 5.61 (d, ^3J = 9 Hz, 3H, NHCHN), 6.98–7.24 (m, 30H, C$_6$H$_5$), 8.20 (m, 6H, NHCHN and NHCH$_2$). – ^{13}C NMR (100.5 MHz, CDCl$_3$): δ = 12.19 [C$_5$(CH_3)$_5$], 37.18, 42.35 and 53.40 (CH$_2$-Gly, CH$_2$-Phe and NHCH-Phe), 62.84 (NHCHN), 127.33, 127.41, 127.88, 128.53, 128.75, 128.87, 131.16, 133.41 and 135.73 [C_5(CH$_3$)$_5$ and Ph], 166.94, 168.30 and 169.80 (CO$_2$ and CON).

6: Synthesis analogous to that for **4**; extraction with dichloromethane/pentane (20 mL) (1:1). Orange powder. Yield 110 mg (49%), m.p. >189 °C (decomp).-IR (KBr): $\tilde{\nu}$ = 1664 cm^{-1} vs (CO$_2$ and CON), 1518 vs (CON). – ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.89 [d, ^3J = 6 Hz, 9H, CH(CH_3)$_2$], 0.94 [d, ^3J = 7 Hz, 9H, CH(CH_3)$_2$], 1.37 [m, 3H, CH(CH$_3$)$_2$], 2.04 (m, 6H, CH$_2$-Leu), 2.13 (s, 15H, Cp*), 2.94 (dd, ^2J = 15, ^3J = 10 Hz, 3H, CH$_2$-Phe), 3.29 (dd, ^2J = 15, ^3J = 5 Hz, 3H, CH$_2$-Phe), 4.63–4.68 (m, 3H, NHCH-Phe), 4.69–4.75 (m, 3H, NHCH-Leu), 5.75 (d, ^3J = 9 Hz, 3H, CH-Gly), 5.83 (d, ^3J = 8 Hz, 3H, NH-Phe), 7.02–7.54 (m, 30H, Ph), 8.39 (d, ^3J = 9 Hz, 3H, NH-Leu), 8.60 (d, ^3J = 9 Hz, 3H, NH-Gly). – ^{13}C NMR (100.5 MHz, CDCl$_3$): δ = 12.10 [C$_5$(CH_3)$_5$], 21.51, 23.53 and 24.84 [CH(CH_3)$_2$ and CH(CH_3)$_2$], 36.99 and 40.38 (CH$_2$-Leu and CH$_2$-Phe), 50.46 and 54.15 (NHCH-Phe and NHCH-Leu), 63.20 (NHCHN), 127.34, 127.52, 127.74, 127.86, 128.56, 128.94, 131.02, 133.42 and 135.34 [C_5(CH$_3$)$_5$ and Ph], 166.65, 167.70 and 171.92 (CO$_2$ and CON).

7: Synthesis analogous to that for **4**; extraction with dichloromethane/acetone (2:1) (30 mL). The slight difficulties in obtaining high-resolution spectra of complexes **4**–**6** became more dominant in compounds **7** and **8**; even at low concentrations only poorly resolved signals can be obtained. Orange powder. Yield 35 mg (13%), m.p. >203 °C (decomp). IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1} vs (CO$_2$ and CON), 1523 vs (CON).

8: Synthesis analogous to that for **4**; extraction with dichloromethane/ether (3:1) (20 mL). Orange powder. Yield 32 mg (6%), m.p. >189 °C (decomp).-IR (KBr): $\tilde{\nu}$ = 1657 cm^{-1} vs (CO$_2$ and CON), 1523 vs (CON).

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[5] Suitable single crystals of **3** were obtained by layering an ethyl acetate solution with hexane. $C_{39}H_{36}N_6O_9Ti \cdot H_2O$; M = 746.64; red fragment; monoclinic; only crystals of relatively poor quality could be found. One phenyl group and the Cp* ring are severely disordered—the disorder could not be resolved; space group $C2/c$ (no. 15); a = 2.3493(2); b = 1.4973(3); c = 2.0238(4) Å; β = 94.879(12)°; V = 7.093(2) nm^3; Z = 8; μ(Mo$_{K\alpha}$) = 2.989 cm^{-1}; ρ_{calcd} = 1.401 g cm^{-3}. Diffractometer Enraf-Nonius CAD4; 291 K; graphite monochromator; scan range (θ): 2–23°; $\pm h$, $-k$, $-l$; scan width: (0.54 + 0.35 tan θ)°; max. measurement time 15 s per reflection; negligible crystal decomposition; empirical absorption correction (psi-scan) T_{min}/T_{max}: 0.92/0.99; 5313 reflections measured/4147 symmetry independent/3450 "observed" for ($|F| > 2\sigma(|F|)$); structure solution with SIR; refinement with SHELXTL-PLUS; H atoms geometrically positioned and refined using the "riding" model; 469 parameters; max./min. residual electron density 0.73/−0.35 e Å^{-3}; R = 0.0689; R_w = 0.0705 [$w^{-1} = \sigma^2(F_0)$]. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-401635.

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