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Gold Compounds

Structural Studies of Gold(I, II, and III) Compounds with Pentafluorophenyl and Tetrahydrothiophene Ligands**

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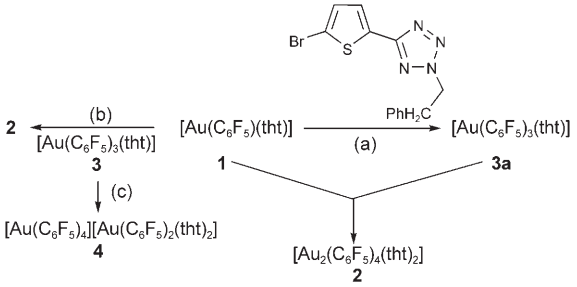
The first tetrahydrothiophene (tht) complex of gold was reported by Cattalini et al. in 1968,[1] and Vaughan and Sheppard were the first to obtain a gold complex that contained the pentafluorophenyl (pfp) group as a ligand two years later.[2] Since then and mainly up to the 1980s, Usón and co-workers—with the Laguna brothers and Vicente prominent—have developed the chemistry of such compounds. The pfp group is now commonly used as a robust and generally inert ligand (compared to other aryl groups), whereas tht, a labile ligand towards gold, is commonly employed for enabling substitution reactions. Several synthetic procedures involving these ligands are described in two books edited by King and Eisch.[3] Later applications are available in various books and review articles.[4] It is surprising that no crystal structure determinations of gold complexes that contain both of these important ligands coordinated to a gold center have been described. Herein, as a tribute to Usón and others, we rectify that shortcoming by reporting for the first time the crystal and molecular structures of both [Au(C_6F_5)(tht)] (**1**) and [Au(C_6F_5)$_3$(tht)] (**3**) as well as an unprecedented example of an unbridged, unchelated dinuclear gold(II) compound, [Au_2(C_6F_5)$_4$(tht)$_2$] (**2**), that could be obtained in a rational manner. Finally, we discuss a unique rearrangement of **3** in solution that effects ionic compound formation between two gold(III) complexes in [Au(C_6F_5)$_4$][Au(C_6F_5)$_2$(tht)$_2$] (**4**). Such mononuclear ligand scrambling, although fairly common for gold(I) compounds, has never before been documented for gold(III) complexes. It is noteworthy, however, that the Fackler and Schmidbaur groups have independently described the ligand dynamics (which involve isomerizations and rearrangements) in various ylide-bridged gold(III) complexes.[5]

As part of an ongoing investigation of preferential gold coordination to various N-heterocycles, [Au(C_6F_5)(tht)] was treated with the organic bromide 5-(5-bromothiophen-2-yl)-2-phenethyl-2*H*-tetrazole in a 1:1 ratio (Scheme 1). This reaction afforded a mixture that contained gold in various oxidation states. From this mixture the gold(II) compound [Au_2(C_6F_5)$_4$(tht)$_2$] (**2**), representing the first example of an unbridged complex with a formal $[Au_2]^{4+}$ core in which the gold centers are not stabilized by any chelating ligands, as well as the gold(III) complex [Au(C_6F_5)$_3$(tht)] (**3a**, one polymorph of compound **3**; see below) were crystallized. Upon standing (ca. 24 h), gold metal was visible in the form of a gold mirror on the walls of the Schlenk tube. In a similar reaction, **1** was treated with 2-bromo-5-methylthiophene, which also resulted in oxidation of the gold(I) precursor to eventually furnish crystals of **3a**. We subsequently prepared the gold(II) compound **2** from an extremely slow redox reaction between equimolar quantities of compounds **1** and **3**. The formation of compound **2** in this reaction could be confirmed by unit-cell determinations with single-crystal X-ray diffraction of various crystals isolated from the mixture. In addition, unreduced [Au(C_6F_5)$_3$(tht)] crystallized unaltered from the solution, thereby effecting the structure **3b** (a second polymorph of compound **3**; see below), while some of **3** underwent spontaneous ligand rearrangement to afford ionic compound **4**, which consists of two gold(III) complexes. Uncertainty as to the existence of **2** in solution exists, since all attempts to obtain NMR spectroscopic data were unsuccessful. Furthermore, FAB mass spectrometric data obtained for crystals of compound **2** also failed to deliver any identifiable peaks.



Scheme 1. Formation of crystalline products **2** and **3a** from reaction (a) (assuming **2** formed from **1** and **3**) and **2** from reaction (b); in (c) **3** rearranges to form **4** and also crystallizes as **3b**.

In the most spectacular of the crystalline pfp–tht complex products, [(C_6F_5)$_2$(tht)Au–Au(tht)(C_6F_5)$_2$] (**2**), the gold atoms occur in two distorted square-planar configurations, featuring an essentially linear S-Au-Au-S axis and two orthogonally oriented {C_6F_5-Au-C_6F_5} moieties with all aromatic rings in parallel planes (Figure 1). The tht ligands are situated at a torsion angle of 93° with respect to each other, on either side of the S1-Au1-Au1′-S1′ backbone. The Au^{II}–Au^{II} bond length (2.5679(7) Å) is within the range of interactions displayed by the only other reported examples of unbridged, but chelated,

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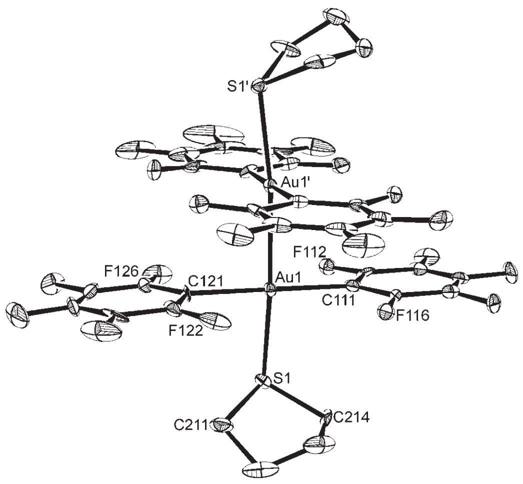

Figure 1. Molecular structure of **2**; thermal ellipsoids are set at 25% probability and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C111-Au1 2.110(2), C121-Au1 2.078(2), S1-Au1 2.418(3), Au1-Au1′ 2.5679(7); S1-Au1-Au1′ 173.58 (7), C111-Au1-S1 90.7(1), C121-Au1-S1 89.9(1), C111-Au1-Au1′ 91.53(6), C121-Au1-Au1′ 88.14(7), C111-Au1-C121 177.6 (2).

$Au^{II}-Au^{II}$ compounds, namely, bis(quinolin-8-ylthio)digold dichloride (2.5355(5) Å),[6] $[Au_2Cl_2(dppn)_2][PF_6]_2$ (2.6112(7) Å; dppn = 1,8-bis(diphenylphosphino)naphthalene),[7] $[Au_2Br_2(dppn)_2][PF_6]_2$ (2.6035(8) Å), and $[Au_2I_2(dppn)_2][PF_6]_2$ (2.6405(8) Å).[8] Furthermore, the Au–C bonds (2.110(2), 2.078(2) Å) are significantly longer than those observed for the anionic gold(I) compound $[Au(C_6F_5)_2][nBu_4N]$ (2.044(4) Å),[9] probably reflecting the higher s character of the overlapping orbitals in gold(I) compared to gold(II).[10] The formation of the dinuclear compound **2** from **1** and **3** can formally be interpreted in terms of C_6F_5 radical transfer from the gold(III) center to the gold(I) center and simultaneous Au–Au bond formation. Few examples of C_6F_5 reactivity in gold complexes, at least in terms of ligand transfer, are known.[11]

Crystals of the gold(III) compound **3** were obtained in two polymorphic forms with both types of crystals featuring similar, equivalent molecules wherein the donor atoms of the ligands occur in a square-planar arrangement about the central gold atoms. Molecular-structure representations of **3a** and **3b** with selected bond lengths and angles are available in the Supporting Information. The only obvious difference between the two polymorphs appears to be the orientation of the tht ligand. Owing to the large mutual *trans* influences of the two opposing pfp ligands, their Au–C bond lengths (≥2.06 Å) are longer than when the pfp ligand is coordinated *trans* to tht (2.035(5), 2.031(3) Å). Similar results have been obtained for $[Au(C_6F_5)_3(S_2CPEt_3)]$[12] and $[AuMe_3PPh_3]$.[13] The Au–C and Au–S bond lengths in compound **3** are in close agreement with those observed in $[Au(C_6F_5)_3(S_2CPEt_3)]$ (2.067(4), 2.076(4), 2.037(3) Å, and 2.366(1) Å, respectively).

Well-documented homoleptic rearrangements of gold(I) complexes occur according to Equation (1) (charges omitted) where X and L correspond to combinations of soft ligands.[14]

$$2\,[\mathrm{AuXL}] \rightleftharpoons [\mathrm{AuX_2}] + [\mathrm{AuL_2}] \qquad (1)$$

We have now established that ligand scrambling also takes place for a mononuclear organogold(III) compound according to Equation (2), and other examples may be discovered in the future.

$$2\,[\mathrm{AuX_3L}] \rightleftharpoons [\mathrm{AuX_4}] + [\mathrm{AuX_2L_2}] \qquad (2)$$
$$(\mathrm{X} = \mathrm{C_6F_5}^-;\ \mathrm{L} = \mathrm{tht})$$

The ionic compound $[Au(C_6F_5)_4][Au(C_6F_5)_2(tht)_2]$ (**4**; Figure 2), the result of such a ligand scrambling, represents the first gold(III) compound containing pfp and/or tht in both of the composite ions. The coordination geometry of both gold atoms is square-planar. The homoleptic anion has the same propeller-like appearance as reported for $[Au(C_6F_5)_4][Ph_3P{=}N{=}PPh_3]$[15] with comparable Au–C bond lengths, ranging from 2.050(6) to 2.065(6) Å. The cation, on the other hand, contains a Au^{III} center of the type *trans*-$[AuR_2L_2]$ (L = neutral ligand, R = anionic organic ligand) comparable to the complex $[Au(C_6F_5)_2(tht)_2]OTf$.[16] The coordination arrangement in the formed cationic complex represents a rare example of a symbiotic relationship between ligands in a square-planar d^8 complex. Furthermore, the very strong preference for *cis* isomers in $[AuR_2X_2]$ compounds (according to the Tobias orbital rationalization)[17] is refuted.

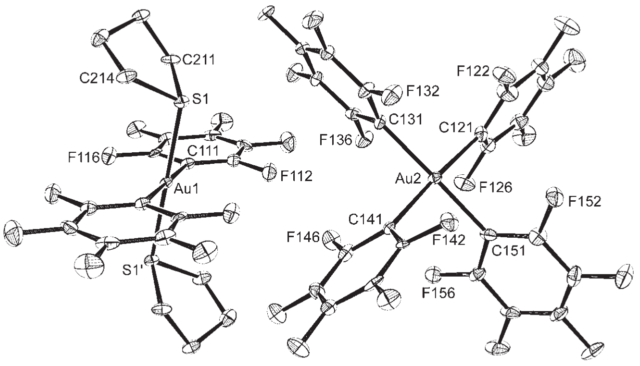

Figure 2. ORTEP representation of **4**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and pentane molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C111-Au1 2.066(6), S1-Au1 2.335(2), C121-Au2 2.051(6), C131-Au2 2.050(6), C141-Au2 2.065(6), C151-Au2 2.055(7); C111-Au1-S1 91.1(2), C111-Au1-S1′ 88.9(2), C111′-Au1-S1 88.9(2), C111′-Au1-S1′ 91.1(2), C111-Au1-C111′ 180.0, S1-Au1-S1′ 180.0, C121-Au2-C131 91.2(3), C121-Au2-C151 87.8(3), C131-Au2-C141 92.3(2), C141-Au2-C151 88.8(2), C121-Au2-C141 176.5(3), C131-Au2-C151 176.4(3).

To complete a series of gold(I, II, and III) compounds $[Au_x(C_6F_5)_y(tht)_z]$, the structure of the important starting compound **1**[18] was determined. The asymmetric unit contains two independent monomers with similar paddle-like geometries. These monomers form an infinite chain along the *a* axis of the crystal through alternating long (3.306 Å) and two different short (3.191, 3.128 Å) aurophilic interactions (Figure 3). All of these separations fall within the range of typically observed separations for aurophilic interactions between gold(I) centers.[16,19] Identical pairs of molecules are alternatingly rotated by 180°. Wide angles (142.8°, 139.2°) between symmetry-related molecules and small torsion

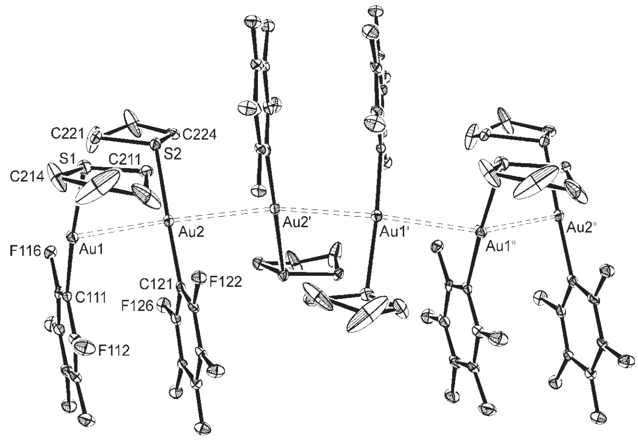

Figure 3. The organization of **1** in an infinite chain along the *a* axis. Thermal ellipsoids are set at 25% probability. Hydrogen atoms and ether molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: C111-Au1 2.014(9), C121-Au2 2.03(1), S1-Au1 2.317(3), S2-Au2 2.320(3), Au1···Au2 3.306(1), Au2···Au2′ 3.191(2), Au1′···Au1″ 3.128(2); C111-Au1-S1 176.3(3), C121-Au2-S2 178.0(3).

angles (42.85°) between the independent monomers are observed.

The small torsion angles of the latter result in greater steric hindrance and weaker Au···Au interactions, as is evident from the observed bond lengths. The Au–S bond lengths present in the structure (2.317(3) and 2.320(3) Å) do not deviate significantly from those observed for $[Au(tht)_2][C_6H_4NO_4S_2]$ (2.292(2) Å) and $[Au(tht)_2][AuI_2]$ (2.306(7), 2.335(6) Å).[20,21] The observed Au–C bond lengths (2.014(9), 2.03(1) Å) can be compared to those in $[Au(C_6F_5)\{S{=}\overline{CN(H)C(CH_3){=}C(H)S}\}]$ (2.06(1) Å).[11]

Herein we have reported the first aryl- and thiophene-containing gold(II) complex, which could be formed by radical transfer and gold–gold bond formation, as well as a gold(I) and two gold(III) compounds that contain the same ligands. One of the latter products resulted from a novel ligand-scrambling (metathesis or disproportionation) reaction. In all the complexes (independent of charge) that contain a $\{C_6F_5\text{-Au-}C_6F_5\}$ unit, the Au–C bond lengths decrease in the order $Au^{II} > Au^{III} > Au^{I}$ (ca. 2.11, 2.06, and 2.04 Å). A similar variation is found for the Au–S separation in the $\{tht\text{-}Au^{III}\text{-}C_6F_5\}$, $\{tht\text{-}Au^{III}\text{-}tht\}$, $\{tht\text{-}Au^{II}\text{-}Au^{II}\}$, and $\{tht\text{-}Au^{I}\text{-}C_6F_5\}$ fragments (ca. 2.36, 2.34, 2.42, and 2.32 Å). Theoretical studies are underway.

Experimental Section

The preparation of compounds **1**–**4** is described in detail in the Supporting Information.

X-ray structure determinations and data collection: Suitable single crystals for X-ray structural analysis were obtained by crystallization from concentrated diethyl ether solutions layered with *n*-hexane or *n*-pentane. Data sets for **1**, **2**, **3**, and **4** were collected on a Bruker SMART Apex CCD difractometer[22] with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data reduction was carried out with standard methods from the software package Bruker SAINT.[23] SMART data were treated with SADABS.[24,25] The structures were solved by direct methods (**1**, **3b**, **4**) or interpretation of a Patterson synthesis (**3a**, **3**), which yielded the position of the metal atoms, and conventional difference Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 using SHELXL-97[26] within the X-seed environment.[27,28] The hydrogen atoms were fixed in calculated positions. X-seed was used to generate the various figures of the complexes.

CCDC-626605–626609 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.[29–31]

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[1] L. Cattalini, M. Martelli, G. Marangoni, *Inorg. Chem.* **1968**, *7*, 1492–1495.
[2] L. G. Vaughan, W. A. Sheppard, *J. Organomet. Chem.* **1970**, *22*, 739–742.
[3] a) R. Usón, A. Laguna in *Organometallic Synthesis, Vol. 3* (Eds.: R. B. King, J. J. Eisch), Elsevier, Amsterdam, **1986**, pp. 322–342; b) R. Usón, A. Laguna in *Organometallic Synthesis, Vol. 4* (Eds.: R. B. King, J. J. Eisch), Elsevier, Amsterdam, **1988**, pp. 342–353.
[4] For example, see: a) M. C. Gimeno, A. Laguna in *Comprehensive Coordination Chemistry II*, *Vol. 6* (Eds.: J. A. McCleverty, T. J. Meyer) 1st ed., Elsevier, Oxford, **2004**, pp. 990–1145; b) A. Grohmann, H. Schmidbaur in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), 1st ed., Elsevier Science, Oxford, **1995**, pp. 1–56.
[5] a) S. Wang, J. P. Fackler, Jr. in *The Chemistry of Organic Derivatives of Gold and Silver*, *Vol. 6* (Eds.: S. Patai, Z. Rappoport) 2nd ed., Wiley, Chichester, **1999**, pp. 431–450; b) H. Schmidbaur, A. Grohmann, M. E. Olmos, A. Schier in *The Chemistry of Organic Derivatives of Gold and Silver*, *Vol. 6* (Eds.: S. Patai, Z. Rappoport), 2nd ed., Wiley, Chichester, **1999**, pp. 271–272.
[6] S. A. Yurin, D. A. Lemenovskii, K. I. Grandberg, I. G. Ll'ina, L. G. Kuz'mina, *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 2752–2753.
[7] V. W. W. Yam, S. W. K. Choi, K. K. Cheung, *Chem. Commun.* **1996**, 1173–1174.
[8] V. W. W. Yam, C. K. Li, C. L. Chan, K. K. Cheung, *Inorg. Chem.* **2001**, *40*, 7054–7058.
[9] P. G. Jones, *Z. Kristallogr.* **1993**, *208*, 347–350.
[10] L. E. Orgel, *J. Chem. Soc.* **1958**, 4186–4190.
[11] S. Cronje, H. G. Raubenheimer, H. S. C. Spies, C. Esterhuysen, H. Schmidbaur, A. Schier, G. J. Kruger, *Dalton Trans.* **2003**, 2859–2866.
[12] R. Usón, A. Laguna, M. Laguna, M. Luz Castilla, P. J. Jones, C. Fittschen, *J. Chem. Soc. Dalton Trans.* **1987**, 3017–3022.
[13] J. Stein, J. P. Fackler, Jr., C. Paparizos, H. W. Chen, *J. Am. Chem. Soc.* **1981**, *103*, 2192–2198.
[14] For example, see: a) S. Ahmad, *Coord. Chem. Rev.* **2004**, *248*, 231–243; b) S. Onaka, Y. Katsukawa, M. Shiotsuka, O. Kanegawa, M. Yamashita, *Inorg. Chim. Acta* **2001**, *312*, 100–110; c) A. L. Hormann-Arendt, C. F. Shaw, *Inorg. Chem.* **1990**, *29*, 4683–4687.
[15] a) P. G. Jones, E. Bembenek, *Z. Kristallogr.* **1994**, *209*, 690–692; b) H. H. Murray, J. P. Fackler, Jr., L. C. Porter, D. A. Briggs, M. A. Guerra, R. J. Lagow, *Inorg. Chem.* **1987**, *26*, 357–363.
[16] F. Mohr, E. Cerrada, M. Laguna, *Organometallics* **2006**, *25*, 644–648.
[17] a) R. J. Puddephatt in *Comprehensive Organometallic Chemistry I*, *Vol. 2* (Eds.: E. J. Abel, F. J. Stone, G. Wilkinson), 2nd ed.,

Pergamon, Oxford, **1982**, p. 762, p. 789, p. 801; b) R. S. Tobias, *Inorg. Chem.* **1970**, *9*, 1296–1298.

[18] R. Usón, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85–91.

[19] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, *24*, 391–400.

[20] S. Friedrichs, P. G. Jones, *Acta Crystallogr. Sect. C* **2000**, *56*, 56–57.

[21] S. Ahrland, B. Norèn, A. Oskarsson, *Inorg. Chem.* **1985**, *24*, 1330–1333.

[22] SMART, Data collection software (version 5.629), Bruker AXS Inc.(Madison), WI, **2003**.

[23] SAINT, Data reduction software (version 6.45), Bruker AXS Inc. (Madison), WI, **2002**.

[24] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.

[25] SADABS (version 2.05), Bruker AXS Inc. (Madison), WI, **2002**.

[26] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Analysis, University of Göttingen (Germany), **1997**.

[27] J. L. Atwood, L. J. Barbour, *Cryst. Growth Des.* **2003**, *3*, 3–8.

[28] L. J. Barbour, *Supramol. Chem.* **2003**, *1*, 189–191.

[29] Crystal data for **1** at 100 K: $C_{10}H_8AuF_5S_1\cdot 0.25\,C_4H_{10}O$, $M_r = 470.72$ g mol^{-1}, colorless needle, orthorhombic, space group *Pbnb* (No. 56), $a = 11.851(5)$, $b = 18.664(8)$, $c = 22.576(9)$ Å, $V = 4994(4)$ Å^3, $Z = 16$, $\rho_{calcd} = 2.504$ g cm^{-3}, $F(000) = 3496$, $\mu(Mo_{K\alpha}) = 11.993$ mm^{-1}, $2\theta_{max} = 56.4°$, 29015 reflections measured, 5819 unique ($R_{int} = 0.1020$), goodness of fit = 0.988, $R_1 = 0.0512$, $wR2 = 0.0863$, R indices based on 3266 reflections with $I > 2\sigma(I)$ (refinement on F^2), 352 parameters, 0 restraints.

[30] Crystal data for **2** at 100 K: $C_{32}H_{16}Au_2F_{20}S_2$, $M_r = 1238.50$ g mol^{-1}, yellow cube, tetragonal, space group $P4_12_12$ (No. 92), $a = 10.8156(8)$, $c = 28.675(4)$ Å, $V = 3354.3(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.452$ g cm^{-3}, $F(000) = 2312$, $\mu(Mo_{K\alpha}) = 9.000$ mm^{-1}, $2\theta_{max} = 51.4°$, 12595 reflections measured, 3102 unique ($R_{int} = 0.0624$), goodness of fit = 1.127, $R_1 = 0.0458$, $wR2 = 0.0900$, R indices based on 2824 reflections with $I > 2\sigma(I)$ (refinement on F^2), 190 parameters, 24 restraints. Absolute structure parameter = 0.06(2) (H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881).

[31] Crystal data for **4** at 100 K: $C_{44}H_{16}Au_2F_{30}S_2\cdot C_5H_{12}$, $M_r = 1644.77$ g mol^{-1}, colorless needle, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.541(3)$, $b = 13.675(3)$, $c = 17.772(4)$ Å, $\alpha = 74.360(4)$, $\beta = 79.626(4)$, $\gamma = 66.427(3)°$, $V = 2467.3(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.214$ g cm^{-3}, $F(000) = 1564$, $\mu(Mo_{K\alpha}) = 6.176$ mm^{-1}, $2\theta_{max} = 52.9°$, 26187 reflections measured, 10081 unique ($R_{int} = 0.0479$), goodness of fit = 1.047, $R_1 = 0.0432$, $wR2 = 0.0946$, R indices based on 8117 reflections with $I > 2\sigma(I)$ (refinement on F^2), 747 parameters, 0 restraints.