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Thiophene C-H activation as a chain-transfer mechanism in ethylene polymerization: Catalytic formation of thienyl-capped polyethylene

Ringelberg, S.N; Meetsma, A.; Hessen, B.; Teuben, J.H; Mettsma, A

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Supporting material

to "Thiophene C-H activation as Chain-Transfer Mechanism in Ethene Polymerization; Catalytic Formation of Thienyl-Capped Polyethene", by S.N. Ringelberg, A. Meetsma, B. Hessen and J.H. Teuben.

Part I: Experimental section

General

All experiments were performed under nitrogen atmosphere using standard glove-box, Schlenk, and vacuum line techniques, unless where mentioned otherwise. Deuterated solvents (Aldrich) were either dried over Na/K alloy and vacuum transferred before use (C_6D_6, THF-d_8) or degassed, flushed with nitrogen and stored over mol. sieves ($C_2D_2Cl_4$). Toluene and pentane were distilled from Na or Na/K alloy before use. Thiophene (Janssen, 99%) was distilled from KOH under nitrogen before use. 2-Alkylthiophenes used as reference were either purchased (2-ethyl, 2-octyl; Lancaster) or prepared (2-butyl, 2-hexyl, 2-decyl) according to Brandsma *et al.* (Brandsma, L.; Verkruijsse, H. D. "Preparative Polar Organometallic Chemistry, Vol. I, Springer Verlag: Berlin, 1987). The following were prepared according to literature procedures: [Cp*$_2$LaH]$_2$ (ref. 2c in the paper), Cp*$_2$YCH(SiMe$_3$)$_2$ (Den Haan *et al. Organometallics* **1986**, *5*, 1726), Cp*$_2$Y(η-H)(η^5,μ^1-CH$_2$C$_5$Me$_4$)YCp* (ref. 3e in the paper). Ethene (AGA 99.5%) was passed over a supported copper scavenger (BASF R 3-11) and mol. sieves (3Å) before being passed to the reactor. NMR spectra were run on Varian Gemini 200, VXR-300 and Unity-500 spectrometers. GC analyses were performed on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC/MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of [Cp*$_2$Y(2-C$_4$H$_3$S)]$_2$ (1).

For the preparation of **1**, the hydride [Cp*$_2$YH]$_2$ was conveniently generated *in situ* through hydrogenolysis of the alkyl Cp*$_2$YCH(SiMe$_3$)$_2$. To a solution of Cp*$_2$YCH(SiMe$_3$)$_2$ (1.98 g, 3.82 mmol) in 50 mL of pentane, 0.5 mL of thiophene (excess) was added. The solution was subsequently stirred under an atmosphere of H$_2$ for 1 h at ambient temperature. Over that period a white precipitate formed. The supernatant was decanted, the solid was rinsed with pentane and dried *in vacuo*. This yielded 1.40 g (1.58 mmol, 83%) of white **1**. Anal.

Calcd for $C_{48}H_{66}Y_2S_2$: C, 65.15; H, 7.52; Y, 20.09. Found: C, 64.91; H, 7.55; Y, 20.01. IR (cm^{-1}): 2726 (w), 1294 (w), 1186 (m), 1069 (w), 1020 (m), 860 (m), 824 (w), 808 (m), 721 (w), 712 (m), 683 (s), 667 (m), 594 (w), 465 (m). When dissolved in THF-d_8, the material gave ^{1}H- and ^{13}C-NMR spectra identical to those of $Cp^*_2Y(2\text{-}C_4H_3S)$(THF) reported earlier. Crystals of compound **1**, with composition $1.C_6H_6$, can be obtained by diffusion of thiophene into a benzene solution of the hydride $Cp^*_2Y(\eta\text{-}H)(\eta^5,\mu^1\text{-}CH_2C_5Me_4)YCp^*$ at ambient temperature. This material was used for the structure determination described below.

Synthesis of [Cp*$_2$La(2-C$_4$H$_3$S)]$_2$ (2)

To a suspension of $[Cp^*_2LaH]_2$ (0.979 g, 2.39 mmol La) in 60 mL of toluene, 0.5 mL of thiophene was added at ambient temperature. This resulted in a yellow solution that was stirred for 15 min. during which the solution was degassed several times (to remove evolving hydrogen). A white solid gradually precipitated. After 15 minutes the solution was concentrated to 15 mL and cooled to -70°C. The supernatant was subsequently decanted and the white solid was dried *in vacuo*. Yield: 0.830 g (1.69 mmol La, 71%).

^{1}H NMR (500 MHz, C_6D_6, 80°C): δ 7.33 (m, 2H, thienyl CH), 7.22 (m, 1H, thienyl CH), 1.95 (s, 30H, Cp*). ^{13}C NMR (125 MHz, C_6D_6, 80°C): δ 194.4 (br s, *ipso* thienyl C), 135.86 (d, 158.5 Hz, thienyl CH), 130.60 (d, 158.5 Hz, thienyl CH), 126.37 (d, 180.7 Hz, thienyl CH), 121.17 (Cp* C), 11.30 (q, 125.6 Hz, Cp* Me). IR (cm^{-1}): 2726 (w), 1192 (m), 1067 (w), 1022 (m), 874 (w), 853 (m), 820 (w), 804 (m), 729 (m), 712 (w), 694 (w), 683 (m), 590 (w), 573 (w), 463 (m).

Reaction of 2 with THF

To an NMR tube with a solution of **2** (7 mg, 14 μmol La) in C_6D_6, 20 μmol of THF was added by microsyringe. This resulted in formation of a species with ^{1}H NMR characteristics similar to $Cp^*_2Y(2\text{-}C_4H_3S)$(THF).

^{1}H NMR (300 MHz, C_6D_6, 25°C): δ 7.85 (d, 4.2 Hz, 1H, =CH-), 7.53 (dd, 4.2 Hz, 2.9 Hz, 1H, =CH-), 7.19 (d, 2.9 Hz, 1H, =CH-), 1.96 (s, 30H, Cp*)

Addition of a similar amount of thiophene to a solution of **2** in C_6D_6 did not lead to significant changes in the spectrum of **2**.

Catalytic conversion of ethene with 2/thiophene

A: Vacuum line experiment

A 50 mL round-bottom flask equipped with a Teflon stopcock was charged in a nitrogen-filled glove-box with 40 mg (81 μmol La) of $[Cp^*_2La(2\text{-thienyl})]_2$ (**2**) and 5 mL of thiophene

(containing 260 μmol/mL of cyclooctane as internal standard), and a Teflon-coated magnetic stir bar. The vessel was connected to a vacuum line, the mixture was degassed and warmed to 80°C. Subsequently 1 atm of ethene was admitted and the mixture was stirred for 12 h at constant pressure. The resulting clear solution was characterized by GC and GC/MS.

For quantification using the cyclooctane internal standard, a reference solution was made of a mixture of measured quantities of cyclooctane and separately prepared 2-n-alkylthiophenes (C_2-C_{10} side chains). This resulted in a response factor calibration line with excellent linearity for the C_2-increments. Results for the experiment described above are:

n in C_n alkyl chain	μmol	$[C_{n+2}]/[C_n]$
2	458	
4	98	0.21
6	34	0.34
8	14	0.42
10	6	0.42
12	3	0.44
14	1	0.45

B: Autoclave experiments

In a nitrogen-filled dry-box, a Büchi 100 mL glass autoclave was charged with 40 mg (81 μmol La) of [Cp*$_2$La(2-thienyl)]$_2$ (2), 5 mL of solvent (either neat thiophene or toluene/thiophene mixtures; the thiophene contains 26 mmol/mL of cyclooctane as internal standard) and a Teflon-coated magnetic stir bar. The reactor was closed and warmed in an oil bath to 80°C. After an equilibration time of 5 min, ethene pressure was admitted and the mixture was stirred for either 2 h or 0.2 h (ethene being fed continuously to the reactor). Subsequently the reactor was vented and the reaction mixture quenched by addition of 5 mL of methanol. Subsequent work-up was performed under aerobic conditions. The solid product was isolated on a glass frit, rinsed repeatedly with acidified acetone and petroleum ether 40-60, and dried at 70°C *in vacuo*.

The solid products were characterized by NMR (for the reactions in neat thiophene) and/or by GPC (reactions at 7.5 bar). In addition, the solutions were sampled direcly after quenching, and analyzed by GC and GC/MS. Only in the reaction mixture of the reaction

performed in neat toluene were linear olefins observed, all other solutions only showed a distribution of 2-alkylthiophenes. The quantification of the soluble part of the reaction mixture produced at 5 bar gave the following:

n in C_n alkyl chain	μmol	$[C_{n+2}]/[C_n]$
2	798	
4	451	0.57
6	331	0.73
8	288	0.87
10	259	0.90
12	233	0.90
14	210	0.90
16	190	0.90
18	169	0.89

The solid products obtained from neat thiophene were characterized by NMR spectroscopy. Spectral data are given below for the reference compound 2-(n-decyl)-thiophene and the product obtained at 2.5 bar ethene pressure. The ^{1}H NMR spectra of the products from neat thiophene at 2.5 bar and 7.5 bar ethene pressure are also provided on a separate sheet (pulse delay 20 seconds; a longer delay time did not change intergrated intensities for the resonances, except for the most downfield shifted thienyl proton which exhibits a particularly slow relaxation).

2-(n-decyl)-thiophene (reference compound). ^{1}H NMR (500 MHz, 95°C, $C_2D_2Cl_4$): δ 7.11 (d, 4.8 Hz, =CH-), 6.93 (m, =CH-), 6.80 (m, =CH-), 2.85 (t, 7.5 Hz, 2H, α-CH_2), 1.71 (m, 2H, β-CH_2), 1.40 (m, 2H, γ-CH_2), 1.31 (12 H, -CH_2-), 0.92 (t, 6.6 Hz, -CH_3). ^{13}C NMR (125 Hz, 95°C, $C_2D_2Cl_4$): δ 145.66 (C *ipso*), 126.41, 123.60, 122.39 (3x =CH-), 31.61, 31.43, 29.68, 29.29, 29.26, 29.02, 28.99, 28.82, 22.38 (9x CH_2), 13.80 (CH_3).

$H(CH_2CH_2)_n(2-C_4H_3S)$ made at 2.5 bar ethene, 80°C, in neat thiophene. ^{1}H NMR (500 MHz, 95°C, $C_2D_2Cl_4$): δ 7.11 (d, 4.8 Hz, =CH-), 6.93 (m, =CH-), 6.80 (m, =CH-), 2.85 (t, 7.5 Hz, α-CH_2), 1.71 (m, β-CH_2), 1.40 (m, γ-CH_2), 1.31 (-CH_2-), 0.92 (t, 6.8 Hz, -CH_3). Contains 5% 2,5-dialkyl-thiophene: δ 6.57 (s, =CH-), 2.76 (t, α-CH_2). Integrated intensities (normalized on 3 H for -CH_3 end group): α-CH_2 (monoalkyl) : α-CH_2 (dialkyl) : β-CH_2 : -$(CH_2)_n$- : -CH_3 = 1.8H : 0.2H : 2.0H : 74H : 3H. ^{13}C NMR (125 Hz, 95°C, $C_2D_2Cl_4$): δ 145.64 (C *ipso*), 126.39,

123.60, 122.38 (3x =CH-), 31.63, 31.43, 29.68 (3x CH_2), 29.41 (-$(CH_2)_n$-), 29.26, 29.07, 29.02, 28.87, 22.37 (5x CH_2), 13.80 (-CH_3).

^{1}H-NMR spectrum of $H(CH_2CH_2)_n(C_4H_3S)$ produced at 80°C in neat thiophene at 2.5 bar ethene pressure. $(C_2D_2Cl_4, 95°C)$
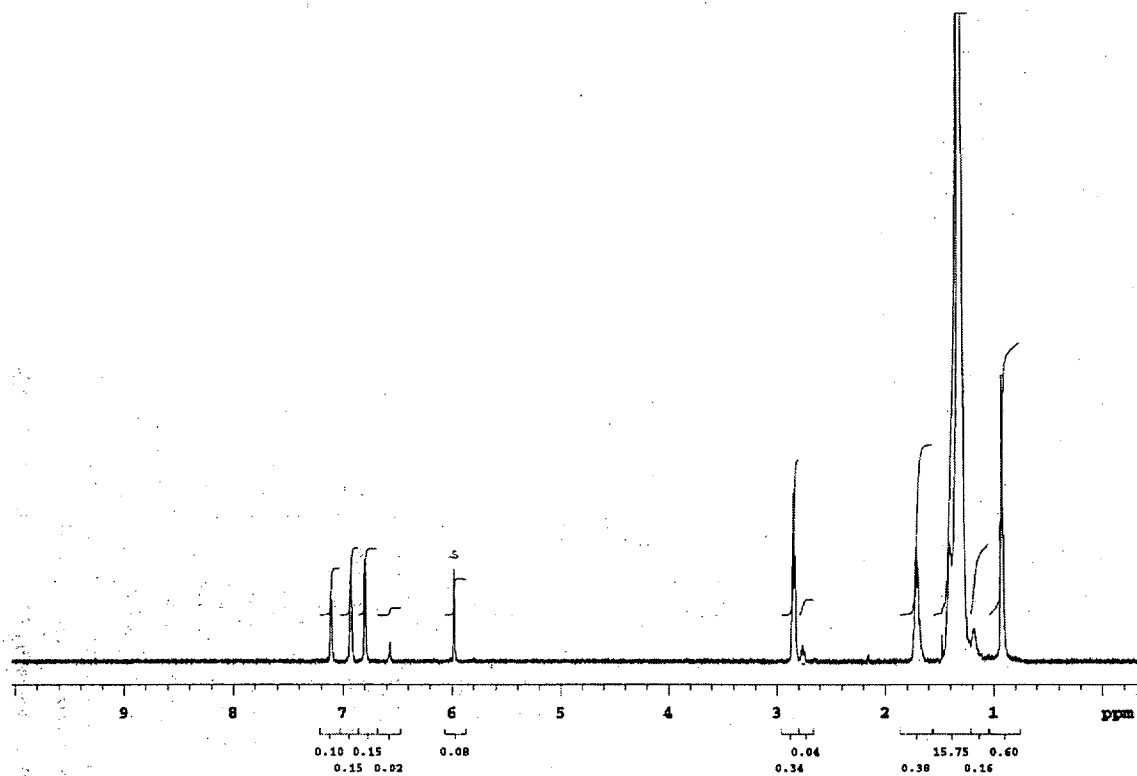
^{1}H-NMR spectrum of $H(CH_2CH_2)_n(C_4H_3S)$ produced at 80°C in neat thiophene at 7.5 bar ethene pressure. $(C_2D_2Cl_4, 95°C)$

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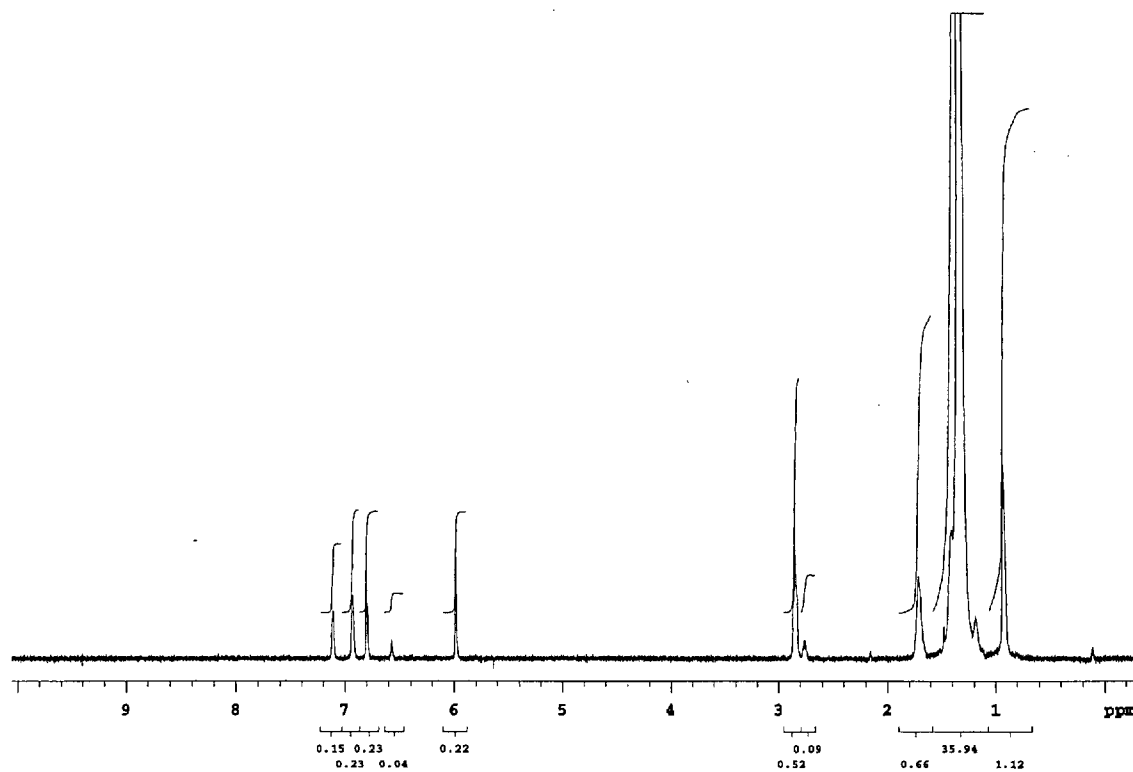
Part II: Structure Determination of [Cp*₂Y(2-thienyl)]₂ (1)

Abstract. $(C_{24}H_{33}SY)_2 \cdot C_6H_6$, M = 963.11, monoclinic, $C2/c$, a = 15.929(1), b = 14.396(1), c = 21.442(1) Å, β = 107.186(6)°, V = 4697.4(5) Å, Z = 4, D_x = 1.362 g cm⁻¹, $\lambda(MoK\bar{\alpha})$ = 0.71073 Å, μ = 25.83 cm⁻¹, F(000) = 2024, T = 130 K, $wR(F^2)$ = 0.2146 for 5193 reflections with $F_o^2 \geq 0$ and 272 parameters and R(F) = 0.0889 for 4112 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

The asymmetric unit consists of two moieties: an half of a dimer of title compound and an half benzene solvent molecule. Both molecules have a crystallographic imposed center of inversion.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Crystals of compound **1**, with composition **1**.C_6H_6, were obtained by diffusion of thiophene into a benzene solution of the hydride $Cp*_2Y(\eta\text{-H})(\eta^5,\mu^1\text{-}CH_2C_5Me_4)YCp*$ at ambient temperature.

The crystal, a parallelepiped of approximate size 0.2x 0.25 0.3 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*[2] diffractometer (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\bar{\alpha}$ radiation, Δω = 0.80 + 0.34 tg θ), interfaced to a *MSDOS* computer.

A few of the reflections found with random search did not fit to the used orientation matrix, indicating some part(s) with misorientation/twinning. It was possible, however, to perform a good structure analysis on this crystal. A search for a crystal of better quality was not successful.

Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 23 reflections in the range 16.05° < θ < 17.88°. The unit cell was identified as monoclinic; reduced cell calculations did not indicate any higher metric lattice symmetry.[5] The space group C2/c was derived from the extinctions. Examination of the final

The intensities of two standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. Two 360° ψ-scan for a reflection close to axial showed a variation in intensity of less than 12% about the mean values. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis showed some of the positions of the hydrogen atoms. Ultimately the hydrogen atoms were included in the final refinement riding on their carrier atoms with $U = c \times U_{equiv}$ of their parent atom, where $c = 1.2$ for the aromatic / non-methyl hydrogen atoms and $c = 1.5$ for the methyl hydrogen atoms and where values U_{equiv} are related to the atoms to which the H atoms are bonded. The methyl-groups were refined as rigid groups, which were allowed to rotate free.

Final refinement converged at $wR(F^2) = 0.2146$ for 5193 reflections with $F_o^2 \geq 0$ and 272 parameters and $R(F) = 0.0889$ for 4112 reflections with $F_o \geq 4.0\ \sigma(F_o)$.

The final difference Fourier map showed a few peaks of max. 2.3 e/Å^3; these are probably caused by the relatively poor crystal quality.

The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2]\ /\ 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates equivalent displacement for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography*.[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

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Legend to the Figure:

Fig. 1.   Perspective *ORTEP*[14] drawing of the title compound with the atom labeling scheme. All atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density. H-atoms have been omitted to improve clarity.

Table 1.

a. Crystal data and details of the structure determination.

Chemical formula	$(C_{24}H_{33}SY)_2 \cdot C_6H_6$
Formula weight, $g.mol^{-1}$	963.11
Crystal system	monoclinic
Space group, no.[16]	C2/c, 15
a, Å	15.929(1)
b, Å	14.396(1)
c, Å	21.442(1)
β, deg	107.186(6)
V, Å	4697.4(5)
Z	4
D_{calc}, $g.cm^{-3}$	1.362
F(000), electrons	2024
$\mu(Mo \, K\overline{\alpha})$, cm^{-1}	25.83
Approx. crystal dimension, mm	0.2 x 0.25 x 0.3

b. Data collection.

Radiation	Mo K$\overline{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.95, 28.0
ω/2θ scan, deg	$\Delta\omega = 0.80 + 0.34\ tg\ \theta$
Data set	h: -20→0; k: 0→18; l: -27→28
Crystal-to-receiving-aperturedistance, mm	173
Horizontal, vertical	
aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	3-1-7, 1.3
r.m.s. dev. in %	0-4-3, 1.4
Drift correction	0.991 - 1.000
X-ray exposure time, h	67.9
Total data	5993
Unique data	5647
Data with criterion: $(F_o \geq 4.0\ \sigma\ (F_o))$	4112
$R_{int} = \sum [|F_o^2 - F_o^2\ (mean)\ |] / \sum [F_o^2]$	0.0310
$R_{sig} = \sum \sigma(F_o^2) / \sum [F_o^2]$	0.0717

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)   5193

Number of refined parameters   272

Final agreement factors:

$wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ 0.2146

    for $F_o^2 > 0$

Weighting scheme: a, b 0.0001, 213

    $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$

    and $P = [max(F_o^2, 0) + 2F_c^2] / 3$

$R(F) = \sum(||F_o| - |F_c||) / \sum|F_o|$ 0.0889

    for $F_o > 4.0\, \sigma\, (F_o)$

GooF = S =

    $= [\sum w [(|F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ 1.135

    n = number of reflections

    p = number of parameters refined

Residual electron density in final

    difference Fourier map, $e/Å^3$ -1.09, 2.28(17)

Max. (shift/σ) final cycle   < 0.001

Max. shift final cycle, Å   < 0.001

Table 2. **Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses.** Atoms of the Asymmetric Unit.

Residue: 1.

Atom	x	y	z	U_{eq} (Å^2)[*]
Y(1)	0.21369(5)	0.21764(5)	0.12128(4)	0.0123(2)
S(1)	0.35291(13)	0.20630(15)	0.05637(10)	0.0179(5)
C(1)	0.1448(5)	0.3518(6)	0.1756(4)	0.018(3)
C(2)	0.2293(5)	0.3375(5)	0.2195(4)	0.015(2)
C(3)	0.2919(5)	0.3633(6)	0.1875(4)	0.018(2)
C(4)	0.2467(5)	0.3982(5)	0.1246(4)	0.015(2)
C(5)	0.1546(5)	0.3907(5)	0.1177(4)	0.017(2)
C(6)	0.0576(6)	0.3399(7)	0.1884(5)	0.030(3)
C(7)	0.2519(7)	0.3200(6)	0.2917(4)	0.028(3)
C(8)	0.3895(6)	0.3643(7)	0.2203(5)	0.027(3)
C(9)	0.2890(6)	0.4424(6)	0.0782(4)	0.024(3)
C(10)	0.0828(6)	0.4319(7)	0.0623(4)	0.026(3)
C(11)	0.2756(6)	0.0801(6)	0.2053(4)	0.019(2)
C(12)	0.2684(6)	0.0424(6)	0.1428(4)	0.020(2)
C(13)	0.1778(6)	0.0337(6)	0.1084(4)	0.020(2)
C(14)	0.1301(6)	0.0696(6)	0.1477(4)	0.018(2)
C(15)	0.1894(6)	0.0957(6)	0.2092(4)	0.019(3)
C(16)	0.3599(6)	0.0892(7)	0.2606(5)	0.031(3)
C(17)	0.3429(6)	-0.0021(6)	0.1231(5)	0.030(3)
C(18)	0.1404(7)	-0.0178(6)	0.0453(4)	0.028(3)
C(19)	0.0323(6)	0.0661(7)	0.1338(5)	0.028(3)
C(20)	0.1648(7)	0.1146(7)	0.2698(4)	0.029(3)
C(21)	0.4547(6)	0.2191(7)	0.1108(4)	0.025(2)
C(22)	0.5057(6)	0.2697(7)	0.0820(5)	0.029(3)
C(23)	0.4591(6)	0.2995(6)	0.0181(4)	0.023(2)
C(24)	0.3719(5)	0.2735(6)	-0.0058(4)	0.017(2)

Residue: 2.

Atom	x	y	z	U_{eq} (Å^2)[*]
C(25)	0.1623(7)	-0.2749(8)	-0.0175(5)	0.039(3)
C(26)	0.1941(8)	-0.2243(9)	-0.0601(5)	0.041(4)
C(27)	0.2196(9)	-0.2997(8)	0.0429(6)	0.045(4)

[*]) $U_{eq} = 1/3\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$

Table 3. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

Y(1)	-S(1)2.951(2)		C(3)	-C(4)1.420(12)
Y(1)	-C(1)2.654(9)		C(3)	-C(8)1.505(13)
Y(1)	-C(2)2.677(8)		C(4)	-C(5)1.434(12)
Y(1)	-C(3)2.631(9)		C(4)	-C(9)1.498(12)
Y(1)	-C(4)2.649(7)		C(5)	-C(10)1.506(12)
Y(1)	-C(5)2.656(7)		C(11)	-C(12)1.419(12)
Y(1)	-C(11)2.662(9)		C(11)	-C(15)1.418(14)
Y(1)	-C(12)2.664(9)		C(11)	-C(16)1.512(14)
Y(1)	-C(13)2.706(9)		C(12)	-C(13)1.419(13)
Y(1)	-C(14)2.661(9)		C(12)	-C(17)1.514(14)
Y(1)	-C(15)2.686(9)		C(13)	-C(14)1.390(13)
Y(1)	-C(24)a2.452(8)		C(13)	-C(18)1.503(12)
S(1)	-C(21)1.705(9)		C(14)	-C(15)1.427(12)
S(1)	-C(24)1.744(9)		C(14)	-C(19)1.498(14)
C(1)	-C(2)1.411(12)		C(15)	-C(20)1.489(13)
C(1)	-C(5)1.412(12)		C(21)	-C(22)1.367(14)
C(1)	-C(6)1.503(13)		C(22)	-C(23)1.418(13)
C(2)	-C(3)1.417(12)		C(23)	-C(24)1.383(13)
C(2)	-C(7)1.503(12)			

Bond angles (deg.)

S(1)	-Y(1)	-C(1)	135.48(19)	C(5)	-Y(1)	-C(15)	120.7(3)
S(1)	-Y(1)	-C(2)	119.92(18)	C(5)	-Y(1)	-C(24)a	80.5(3)
S(1)	-Y(1)	-C(3)	89.81(19)	C(11)	-Y(1)	-C(12)	30.9(3)
S(1)	-Y(1)	-C(4)	84.03(19)	C(11)	-Y(1)	-C(13)	50.7(3)
S(1)	-Y(1)	-C(5)	110.34(18)	C(11)	-Y(1)	-C(14)	50.9(3)
S(1)	-Y(1)	-C(11)	95.6(2)	C(11)	-Y(1)	-C(15)	30.7(3)
S(1)	-Y(1)	-C(12)	77.1(2)	C(11)	-Y(1)	-C(24)a	134.9(3)
S(1)	-Y(1)	-C(13)	93.6(2)	C(12)	-Y(1)	-C(13)	30.6(3)
S(1)	-Y(1)	-C(14)	123.3(2)	C(12)	-Y(1)	-C(14)	50.5(3)
S(1)	-Y(1)	-C(15)	125.4(2)	C(12)	-Y(1)	-C(15)	50.7(3)
S(1)	-Y(1)	-C(24)a	78.3(2)	C(12)	-Y(1)	-C(24)a	106.3(3)
C(1)	-Y(1)	-C(2)	30.7(3)	C(13)	-Y(1)	-C(14)	30.0(3)
C(1)	-Y(1)	-C(3)	51.3(3)	C(13)	-Y(1)	-C(15)	50.4(3)
C(1)	-Y(1)	-C(4)	51.6(3)	C(13)	-Y(1)	-C(24)a	84.8(3)
C(1)	-Y(1)	-C(5)	30.8(3)	C(14)	-Y(1)	-C(15)	30.9(3)
C(1)	-Y(1)	-C(11)	111.3(3)	C(14)	-Y(1)	-C(24)a	95.3(3)
C(1)	-Y(1)	-C(12)	140.3(3)	C(15)	-Y(1)	-C(24)a	126.2(3)
C(1)	-Y(1)	-C(13)	130.9(3)	Y(1)	-S(1)	-C(21)	111.5(3)
C(1)	-Y(1)	-C(14)	101.0(3)	Y(1)	-S(1)	-C(24)	130.8(3)
C(1)	-Y(1)	-C(15)	90.2(3)	C(21)	-S(1)	-C(24)	96.8(4)
C(1)	-Y(1)	-C(24)a	103.1(3)	Y(1)	-C(1)	-C(2)	75.5(5)
C(2)	-Y(1)	-C(3)	31.0(2)	Y(1)	-C(1)	-C(5)	74.7(5)
C(2)	-Y(1)	-C(4)	51.3(2)	Y(1)	-C(1)	-C(6)	121.4(6)
C(2)	-Y(1)	-C(5)	50.8(2)	C(2)	-C(1)	-C(5)	108.2(7)
C(2)	-Y(1)	-C(11)	91.0(2)	C(2)	-C(1)	-C(6)	127.8(8)
C(2)	-Y(1)	-C(12)	121.6(2)	C(5)	-C(1)	-C(6)	123.6(8)
C(2)	-Y(1)	-C(13)	132.8(2)	Y(1)	-C(2)	-C(1)	73.8(5)
C(2)	-Y(1)	-C(14)	106.5(2)	Y(1)	-C(2)	-C(3)	72.7(5)
C(2)	-Y(1)	-C(15)	82.4(2)	Y(1)	-C(2)	-C(7)	129.8(5)
C(2)	-Y(1)	-C(24)a	131.0(3)	C(1)	-C(2)	-C(3)	107.9(7)
C(3)	-Y(1)	-C(4)	31.2(3)	C(1)	-C(2)	-C(7)	127.0(8)
C(3)	-Y(1)	-C(5)	51.3(3)	C(3)	-C(2)	-C(7)	123.6(8)
C(3)	-Y(1)	-C(11)	101.9(3)	Y(1)	-C(3)	-C(2)	76.3(5)
C(3)	-Y(1)	-C(12)	125.6(3)	Y(1)	-C(3)	-C(4)	75.1(5)
C(3)	-Y(1)	-C(13)	152.5(3)	Y(1)	-C(3)	-C(8)	121.3(6)
C(3)	-Y(1)	-C(14)	135.3(3)	C(2)	-C(3)	-C(4)	108.7(7)
C(3)	-Y(1)	-C(15)	106.6(3)	C(2)	-C(3)	-C(8)	123.6(8)
C(3)	-Y(1)	-C(24)a	122.5(3)	C(4)	-C(3)	-C(8)	127.2(8)
C(4)	-Y(1)	-C(5)	31.4(3)	Y(1)	-C(4)	-C(3)	73.7(5)
C(4)	-Y(1)	-C(11)	132.9(3)	Y(1)	-C(4)	-C(5)	74.6(4)
C(4)	-Y(1)	-C(12)	150.7(3)	Y(1)	-C(4)	-C(9)	121.6(5)
C(4)	-Y(1)	-C(13)	175.8(2)	C(3)	-C(4)	-C(5)	106.7(7)
C(4)	-Y(1)	-C(14)	152.6(3)	C(3)	-C(4)	-C(9)	125.4(8)
C(4)	-Y(1)	-C(15)	133.7(3)	C(5)	-C(4)	-C(9)	127.6(7)
C(4)	-Y(1)	-C(24)a	91.3(3)	Y(1)	-C(5)	-C(1)	74.5(5)
C(5)	-Y(1)	-C(11)	140.7(3)	Y(1)	-C(5)	-C(4)	74.0(4)
C(5)	-Y(1)	-C(12)	171.1(3)	Y(1)	-C(5)	-C(10)	124.9(6)
C(5)	-Y(1)	-C(13)	148.5(3)	C(1)	-C(5)	-C(4)	108.3(7)
C(5)	-Y(1)	-C(14)	124.2(3)	C(1)	-C(5)	-C(10)	126.5(8)

C(4)	-C(5)	-C(10)	124.5(7)	Y(1)	-C(14)	-C(13)	76.8(5)
Y(1)	-C(11)	-C(12)	74.6(5)	Y(1)	-C(14)	-C(15)	75.5(5)
Y(1)	-C(11)	-C(15)	75.6(5)	Y(1)	-C(14)	-C(19)	122.7(6)
Y(1)	-C(11)	-C(16)	122.1(6)	C(13)	-C(14)	-C(15)	109.1(8)
C(12)	-C(11)	-C(15)	107.9(8)	C(13)	-C(14)	-C(19)	126.1(8)
C(12)	-C(11)	-C(16)	125.4(9)	C(15)	-C(14)	-C(19)	123.9(8)
C(15)	-C(11)	-C(16)	126.2(8)	Y(1)	-C(15)	-C(11)	73.7(5)
Y(1)	-C(12)	-C(11)	74.5(5)	Y(1)	-C(15)	-C(14)	73.6(5)
Y(1)	-C(12)	-C(13)	76.3(5)	Y(1)	-C(15)	-C(20)	128.5(6)
Y(1)	-C(12)	-C(17)	126.5(6)	C(11)	-C(15)	-C(14)	107.0(8)
C(11)	-C(12)	-C(13)	108.1(8)	C(11)	-C(15)	-C(20)	126.1(8)
C(11)	-C(12)	-C(17)	125.0(8)	C(14)	-C(15)	-C(20)	125.6(9)
C(13)	-C(12)	-C(17)	125.3(8)	S(1)	-C(21)	-C(22)	108.7(7)
Y(1)	-C(13)	-C(12)	73.1(5)	C(21)	-C(22)	-C(23)	112.7(9)
Y(1)	-C(13)	-C(14)	73.2(5)	C(22)	-C(23)	-C(24)	117.3(8)
Y(1)	-C(13)	-C(18)	126.2(6)	S(1)	-C(24)	-C(23)	104.4(6)
C(12)	-C(13)	-C(14)	107.8(7)	S(1)	-C(24)	-Y(1)a	129.1(4)
C(12)	-C(13)	-C(18)	125.7(9)	C(23)	-C(24)	-Y(1)a	123.9(6)
C(14)	-C(13)	-C(18)	125.9(9)				

Residue: 2.

Interatomic Distances (Å)

C(25) -C(26) 1.377(16)   C(26) -C(27)b   1.358(19)

C(25) -C(27) 1.393(16)

Bond angles (deg.)

C(26)   -C(25)   -C(27)   119.0(11)   C(25)   -C(27)   -C(26)b   121.3(11)

C(25)   -C(26)   -C(27)b   119.7(10)

label *a* indicates symmetry operation: 1/2-*x*, 1/2-*y*, -*z*

label *b* indicates symmetry operation: 1/2-*y*, -1/2-*x*, *z*.