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Methylene bis(dithiobenzoate)

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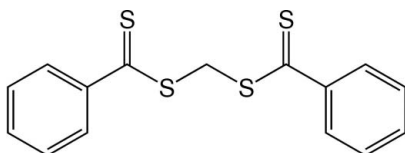
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å;
 R factor = 0.056; wR factor = 0.157; data-to-parameter ratio = 15.1.

In the title compound, $\text{C}_{15}\text{H}_{12}\text{S}_4$, two phenyldithiocarboxylate units are linked through a methylene C atom on a twofold rotation axis. The central $\text{S}-\text{CH}_2-\text{S}$ angle of 116.9 (5)° is significantly larger than the ideal tetrahedral value. The dihedral angle formed by the two phenyl rings is 68.2 (1)°. The refined Flack parameter of 0.2 (3) does not permit unambiguous determination of the absolute structure.

Related literature

For related structures, see: Shrivastav *et al.* (2002); Gonzalez-Castro *et al.* (2000); Quintanilla *et al.* (2005).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{12}\text{S}_4$
 $M_r = 320.49$
Orthorhombic, $P2_12_12$

$a = 11.5800$ (3) Å
 $b = 14.6440$ (11) Å
 $c = 4.2710$ (7) Å

$V = 724.27$ (13) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.64$ mm⁻¹
 $T = 200$ (2) K
 $0.11 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*SORTAV*; Blessing, 1995)
 $T_{\min} = 0.933$, $T_{\max} = 0.987$

5256 measured reflections
1317 independent reflections
931 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.157$
 $S = 1.13$
1317 reflections
87 parameters
H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³
Absolute structure: Flack (1983),
505 Friedel pairs
Flack parameter: 0.2 (3)

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: B12313).

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Gonzalez-Castro, A., Gutierrez-Perez, R., Penieres-Carrillo, G., Diaz-Torres, E., Toscano, R. A., Moya-Cabrera, M., Cabrera-Ortiz, C. & Alvarez-Toledano, C. (2000). *Heteroatom. Chem.* **11**, 120–128.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Quintanilla, M. G., Guerra, E., Dotor, J., Maresova, J., Barba, F. & Martin, A. (2005). *Phosphorus Sulfur Silicon Relat. Elem.* **180**, 1691–1699.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Shrivastav, A., Singh, N. K. & Srivastava, G. (2002). *Bioorg. Med. Chem.* **10**, 2693–2704.

supporting information

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Methylene bis(dithiobenzoate)

Yao-Ren Liang, Hung-Chun Tong, Yih-Hsing Lo, Chia-Her Lin and Ting Shen Kuo

S1. Comment

During studies on the reactivity of the RuS₂ complex {Ru(Tp)(PPh₃)[S₂CC₆H₅]}, (hydridotripyrazol-1-ylborato- κ^3N^2,N^2',N^2'')(phenyldithiocarboxylato- κ^2S,S')(triphenylphosphine- κP)ruthenium, with CH₃CN in dichloromethane, we unexpectedly obtained crystals of the title compound. It consists of two phenyldithiocarboxylate units bridged by a methylene group. The ¹H NMR spectrum in CDCl₃ shows one singlet at 5.31 ppm, assignable to SCH₂S. The EI mass spectrum shows the molecular ion [C₁₅H₁₂S₄]⁺ with the characteristic isotopic distribution patterns. In the crystal, the C2—S2 bond length of 1.643 (6) Å is slightly longer than expected for a C=S double bond (*ca* 1.61 Å), while the C2—S1 and C1—S1 distances of 1.743 (6) and 1.794 (5) Å, respectively, are clearly single bonds. The S—C—S angle of 116.9 (5)° is larger than the ideal tetrahedral value, probably due to repulsion between the CS₂ groups.

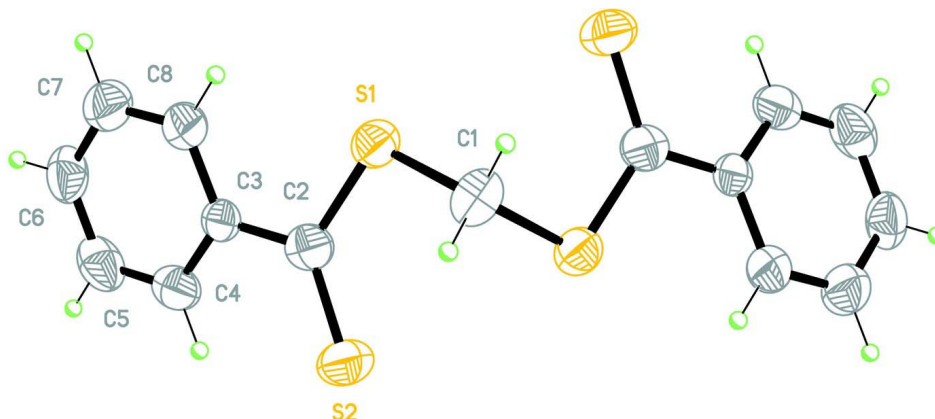
S2. Experimental

The title compound was obtained unexpectedly during studies on the reactivity of {Ru(Tp)(PPh₃)[S₂CC₆H₅] with CH₃CN in dichloromethane. To a solution of {Ru(Tp)(PPh₃)[S₂CC₆H₅] (2.00 g, 2.73 mmol) in CH₂Cl₂ (20 ml), an excess of CH₃CN (2 ml) was added. The resulting yellow solution was heated to reflux for 3 h and the yellow precipitate obtained was filtered and washed with methanol and water to remove excess reagents. The compound was then dried under vacuum to give 0.83 g (91% yield). Crystals for X-ray structure analysis were obtained by recrystallization of the crude product from dichloromethane–hexane.

Elemental analysis calculated: C, 56.21; H, 3.77%; found: C, 56.19; H, 3.69%. ¹H NMR (CDCl₃, 303 K, ppm): δ 7.98–7.35 (m, 10H, Ph), 5.31 (s, 2H, CH₂). MS (*m/z*): 320.5 (*M*⁺).

S3. Refinement

H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.95–0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The refined Flack parameter of 0.2 (3) does not permit unambiguous determination of the absolute structure.

**Figure 1**

Molecular structure of the title compound showing displacement ellipsoids at the 50% probability level for non-H atoms. Non-labelled atoms are related to labelled atoms by the symmetry code 1-x, 2-y, z.

Methylene bis(dithiobenzoate)

Crystal data

$C_{15}H_{12}S_4$
 $M_r = 320.49$
 Orthorhombic, $P2_12_12$
 Hall symbol: P 2 2ab
 $a = 11.5800$ (3) Å
 $b = 14.6440$ (11) Å
 $c = 4.2710$ (7) Å
 $V = 724.27$ (13) Å³
 $Z = 2$

$F(000) = 332$
 $D_x = 1.470$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 5256 reflections
 $\theta = 2.0$ – 25.4°
 $\mu = 0.64$ mm⁻¹
 $T = 200$ K
 Plate, yellow
 $0.11 \times 0.08 \times 0.02$ mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.933$, $T_{\max} = 0.987$

5256 measured reflections
 1317 independent reflections
 931 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$
 $\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -13 \rightarrow 13$
 $k = -17 \rightarrow 17$
 $l = -5 \rightarrow 4$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.157$
 $S = 1.13$
 1317 reflections
 87 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0733P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.46$ e Å⁻³
 Absolute structure: Flack (1983), 505 Friedel
 pairs
 Absolute structure parameter: 0.2 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.47264 (14)	0.89784 (9)	0.5726 (3)	0.0446 (5)
S2	0.72612 (15)	0.92562 (10)	0.5091 (5)	0.0613 (6)
C1	0.5000	1.0000	0.792 (2)	0.049 (2)
H1A	0.4346	1.0109	0.9253	0.058*
C2	0.6098 (5)	0.8635 (4)	0.4525 (14)	0.0437 (15)
C3	0.6104 (5)	0.7734 (4)	0.2900 (15)	0.0381 (14)
C4	0.7071 (5)	0.7447 (4)	0.1238 (15)	0.0480 (17)
H4A	0.7733	0.7828	0.1147	0.058*
C5	0.7082 (6)	0.6617 (4)	−0.0279 (16)	0.0572 (18)
H5A	0.7749	0.6428	−0.1397	0.069*
C6	0.6127 (6)	0.6064 (4)	−0.0173 (15)	0.0562 (18)
H6A	0.6136	0.5491	−0.1211	0.067*
C7	0.5161 (6)	0.6336 (4)	0.1422 (16)	0.0600 (19)
H7A	0.4503	0.5949	0.1492	0.072*
C8	0.5140 (6)	0.7159 (4)	0.2913 (15)	0.0499 (17)
H8A	0.4459	0.7345	0.3977	0.060*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0456 (9)	0.0410 (8)	0.0472 (9)	−0.0042 (7)	0.0029 (7)	0.0005 (7)
S2	0.0472 (10)	0.0568 (9)	0.0800 (14)	−0.0132 (7)	−0.0145 (9)	0.0109 (10)
C1	0.063 (7)	0.043 (5)	0.039 (5)	−0.008 (4)	0.000	0.000
C2	0.042 (4)	0.048 (3)	0.041 (3)	−0.003 (2)	−0.012 (3)	0.017 (3)
C3	0.035 (3)	0.035 (3)	0.044 (4)	0.001 (3)	0.000 (3)	0.016 (3)
C4	0.038 (4)	0.058 (4)	0.048 (4)	0.002 (3)	0.002 (3)	0.018 (3)
C5	0.055 (4)	0.062 (4)	0.054 (4)	0.019 (3)	0.016 (4)	0.011 (4)
C6	0.068 (5)	0.039 (3)	0.062 (4)	0.013 (3)	0.012 (4)	−0.001 (4)
C7	0.057 (5)	0.046 (3)	0.077 (5)	−0.001 (3)	0.017 (4)	−0.005 (3)
C8	0.044 (4)	0.042 (3)	0.064 (4)	0.003 (3)	0.008 (4)	0.001 (3)

Geometric parameters (\AA , $^\circ$)

S1—C2	1.743 (6)	C4—H4A	0.950
S1—C1	1.794 (5)	C5—C6	1.370 (9)
S2—C2	1.643 (6)	C5—H5A	0.950

C1—S1 ⁱ	1.794 (5)	C6—C7	1.369 (8)
C1—H1A	0.960	C6—H6A	0.950
C2—C3	1.491 (8)	C7—C8	1.364 (8)
C3—C4	1.391 (8)	C7—H7A	0.950
C3—C8	1.399 (8)	C8—H8A	0.950
C4—C5	1.377 (9)		
C2—S1—C1	103.5 (2)	C6—C5—C4	119.9 (6)
S1—C1—S1 ⁱ	116.9 (5)	C6—C5—H5A	120.1
S1—C1—H1A	108.0	C4—C5—H5A	120.1
S1 ⁱ —C1—H1A	108.0	C7—C6—C5	120.3 (6)
C3—C2—S2	123.6 (4)	C7—C6—H6A	119.9
C3—C2—S1	113.4 (4)	C5—C6—H6A	119.9
S2—C2—S1	123.0 (4)	C8—C7—C6	120.2 (7)
C4—C3—C8	117.5 (6)	C8—C7—H7A	119.9
C4—C3—C2	120.6 (5)	C6—C7—H7A	119.9
C8—C3—C2	121.8 (5)	C7—C8—C3	121.1 (6)
C5—C4—C3	121.0 (6)	C7—C8—H8A	119.5
C5—C4—H4A	119.5	C3—C8—H8A	119.5
C3—C4—H4A	119.5		
C2—S1—C1—S1 ⁱ	78.0 (2)	C2—C3—C4—C5	-179.7 (5)
C1—S1—C2—C3	174.1 (4)	C3—C4—C5—C6	0.3 (9)
C1—S1—C2—S2	-6.7 (5)	C4—C5—C6—C7	0.3 (10)
S2—C2—C3—C4	-12.4 (8)	C5—C6—C7—C8	0.2 (10)
S1—C2—C3—C4	166.7 (5)	C6—C7—C8—C3	-1.3 (10)
S2—C2—C3—C8	169.3 (5)	C4—C3—C8—C7	1.8 (9)
S1—C2—C3—C8	-11.6 (7)	C2—C3—C8—C7	-179.8 (6)
C8—C3—C4—C5	-1.4 (9)		

Symmetry code: (i) $-x+1, -y+2, z$.