

Methyl 3-(2-hydroxybenzylidene)-2-methyldithiocarbazate

S. K. S. Hazari,^a Sebastian Suarez,^b Biplab Ganguly,^a Fabio Doctorovich^b and Tapashi G. Roy^{a*}

^aUniversity of Chittagong, Chittagong 4331, Bangladesh, and ^bDepartamento de Química Inorgánica, Analítica y Química, Física/INQUIMAE-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Argentina
Correspondence e-mail: tapashir57@gmail.com

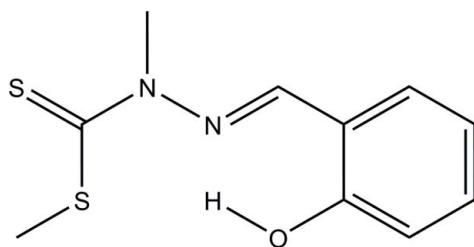
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.053; wR factor = 0.171; data-to-parameter ratio = 19.7.

In the title compound, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{OS}_2$, the thione and S-methyl groups are *syn*. An intramolecular bifurcated $\text{O}-\text{H}\cdots(\text{S},\text{N})$ hydrogen bond occurs.

Related literature

For the biological activity of sulfur-ligand compounds, see: French & Blang (1965); Ali & Livingstone (1974); Ali *et al.* (1995); Hazari *et al.* (1999, 2002). For the synthesis and characterization of sulfur–nitrogen-containing ligands, see: Hazari *et al.* (2002, 2006). For a related structure, see: Hazari *et al.* (2012).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{OS}_2$
 $M_r = 240.34$
Monoclinic, $P2_1/c$
 $a = 11.3561$ (16) Å
 $b = 8.9033$ (13) Å
 $c = 11.5045$ (16) Å
 $\beta = 91.411$ (13)°

$V = 1162.8$ (3) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.43$ mm⁻¹
 $T = 298$ K
 $0.35 \times 0.30 \times 0.22$ mm

Data collection

Oxford Diffraction Gemini CCD S
Ultra diffractometer
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford
Diffraction, 2009)
 $T_{\min} = 0.859$, $T_{\max} = 0.917$
16680 measured reflections
2833 independent reflections
2039 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.171$
 $S = 1.05$
2833 reflections
144 parameters
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.42$ e Å⁻³
 $\Delta\rho_{\min} = -0.41$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1O}\cdots\text{S2}$	0.91 (5)	2.67 (5)	3.453 (2)	145 (4)
$\text{O1}-\text{H1O}\cdots\text{N1}$	0.91 (5)	1.88 (5)	2.678 (3)	145 (4)

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2064).

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supporting information

Acta Cryst. (2012). E68, o1533 [https://doi.org/10.1107/S160053681201731X]

Methyl 3-(2-hydroxybenzylidene)-2-methyldithiocarbamate

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S1. Comment

It is well known that sulfur-containing compounds have potential biological activities (French & Blang, 1965; Ali & Livingstone, 1974; Ali *et al.*, 1995; Hazari *et al.*, 1999; Hazari *et al.*, 2002). As a continuation of the synthesis and characterization of sulfur-nitrogen containing ligands (Hazari *et al.*, 1999; Hazari *et al.*, 2002) and their metal complexes, the present investigation is an attempt to prepare a complex of vanadium(IV) with the Schiff base ligand (*L*, prepared by the condensation of salicylaldehyde and *N*-methyl-S-methyldithiocarbamate). Although a greenish yellow complex was obtained, during crystallization from ethanol, the ligand (m.p. 126–128°C) was regenerated in the form of a crystal. Hence, the crystal structure of the ligand has been described.

In the crystal structure of (1) (Fig.1), there is a bifurcated hydrogen bond involving O1 - H10 $\cdots$ S2 and O1 - H10 $\cdots$ N1 interactions. The O1 S2 and O1 N1 distances are 3.453 (2) Å and 2.678 (3) Å respectively.

S2. Experimental

The title compound was isolated by following four steps synthetic procedure:

Step1. Synthesis of *N*-methyl-S-methyldithiocarbamate: Potassium hydroxide (11.5 g) was dissolved in 60 ml of 90% ethanol and the mixture was cooled down to 273 K in an ice bath. To this, methylhydrazine (11.1 ml) was added slowly with mechanical stirring. A solution of carbondisulfide (12 ml) was added dropwise from a burette with constant stirring over a period of an hour. During the addition of carbondisulfide, the temperature of the reaction mixture was not allowed to rise above 279 K. A yellow colored solution was obtained. After adding carbondisulfide, methyl iodide (12.5 ml) was added from a burette dropwise with vigorous mechanical stirring. After the complete addition, the mixture was stirred for further 15 minutes, whereupon well formed shining crystals appeared. The product was separated by filtration and washed with water and recrystallized from ethanol and dried in a vacuum desiccator over silica gel. Yield: 15.25 g, *M.pt.*: 361–363 K.

Step 2. Synthesis of methyl-*N*-(2-hydroxybenzylidene)-*N*-methyl hydrazinecarbodithionate, *L* (1): A hot solution of salicylaldehyde (1.04 ml, 10 mmol) in absolute ethanol (40 ml) was mixed with hot solution of *N*-methyl-S-methyldithiocarbamate (1.36 g, 10 mmol) in the same solvent. The mixture was refluxed for 6 h. on a water bath. After reducing the volume, a yellowish white product appeared which was filtered off. This product was washed with ethanol several times (3 x 2 ml) and dried in a vacuum desiccator over silica gel. Yield: 1.65 g. *M.pt.*: 399–401 K.

Step 3. Attempted preparation of the oxovanadium(IV) complex with (I): Vanadyl acetylacetonate [VO₂(acac)₂] (2.65 g, 10 mmol) was dissolved in dry ethanol, in which a hot solution of *L* (2.4 g, 10 mmol) in dry ethanol was added. The mixture was refluxed for 6 h. on water bath. After reducing the volume and standing over night a light greenish yellow product appeared, which was washed with ethanol for several times and dried in a vacuum desiccator over silica gel. Melting point of product was 443–445 K.

Step 4. Crystallization: The product was dissolved in ethanol to which half volume of petroleum ether was added (10/5 ml v/v). The solution was left for several days after which the title compound, (I), was deposited as crystals.

S3. Refinement

Methyl groups were idealized ($C-H = 0.96 \text{ \AA}$) and allowed to ride. In all cases, H-atom displacement parameters were taken as $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups or $1.2U_{eq}(C, O)$ otherwise.

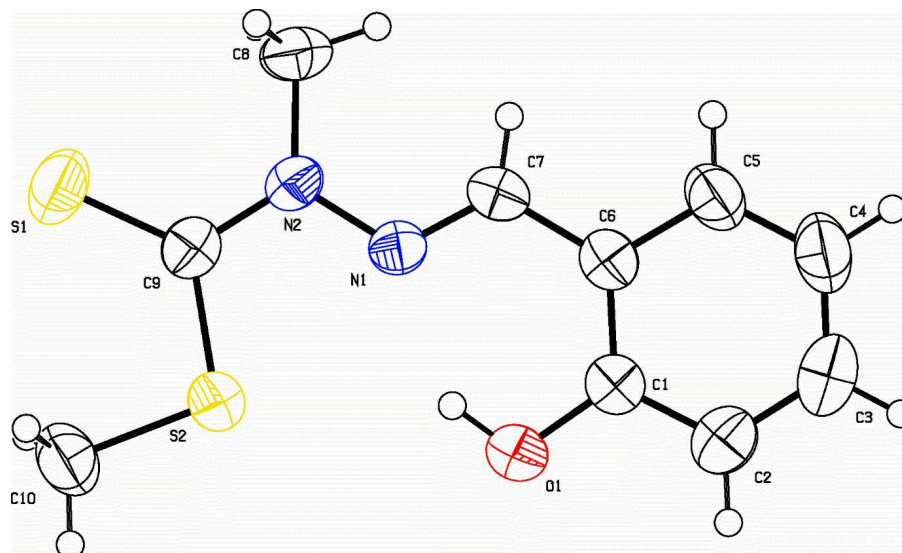


Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

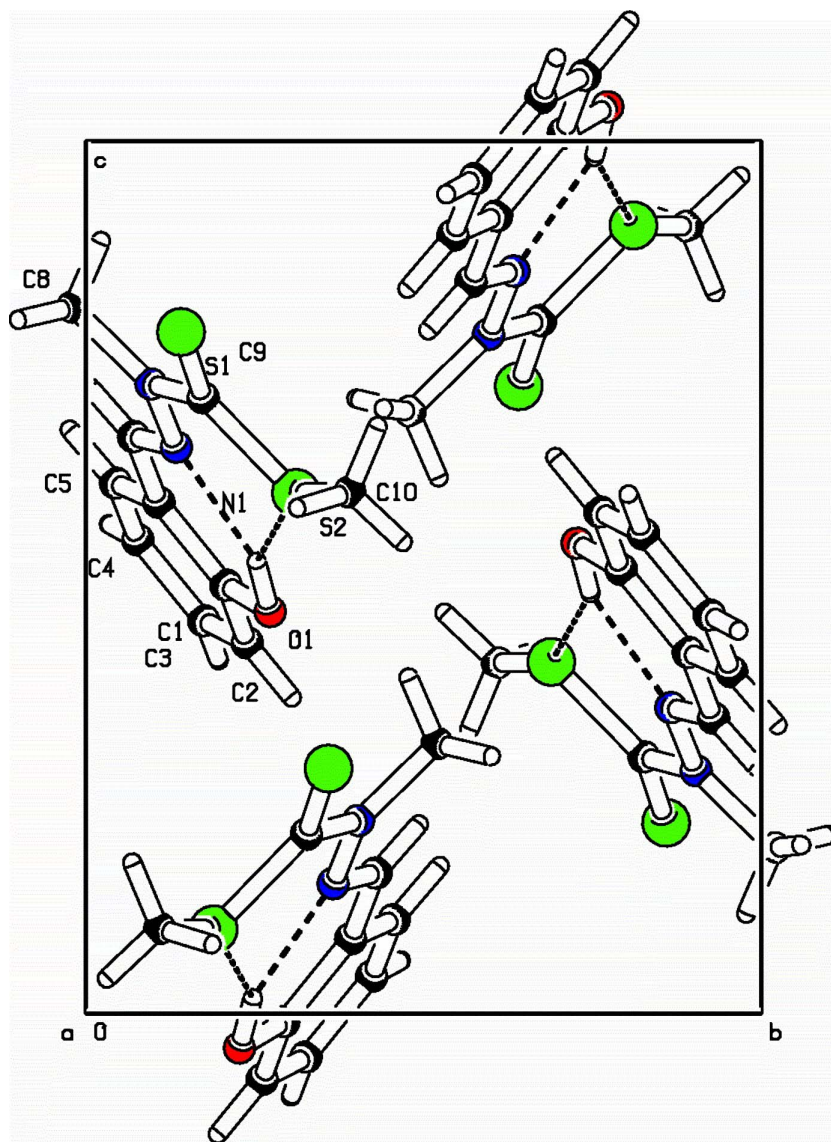


Figure 2

Crystal packing for the title compound viewed along *c*.

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Crystal data

$C_{10}H_{12}N_2OS_2$

$M_r = 240.34$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 11.3561(16)\text{ \AA}$

$b = 8.9033(13)\text{ \AA}$

$c = 11.5045(16)\text{ \AA}$

$\beta = 91.411(13)^\circ$

$V = 1162.8(3)\text{ \AA}^3$

$Z = 4$

$F(000) = 504$

$D_x = 1.373\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$

Cell parameters from 0 reflections

$\theta = 4.0\text{--}29.1^\circ$

$\mu = 0.43\text{ mm}^{-1}$

$T = 298\text{ K}$

Prism, colourless

$0.35 \times 0.30 \times 0.22\text{ mm}$

Data collection

Oxford Diffraction Gemini CCD S Ultra
diffractometer
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.859$, $T_{\max} = 0.917$
16680 measured reflections

2833 independent reflections
2039 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 4.0^\circ$
 $h = -14 \rightarrow 15$
 $k = -11 \rightarrow 11$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.171$
 $S = 1.05$
2833 reflections
144 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 atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0801P)^2 + 0.6976P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S2	0.74513 (6)	0.31081 (8)	0.59687 (6)	0.0526 (2)
S1	0.88032 (7)	0.14078 (11)	0.78107 (8)	0.0705 (3)
O1	0.47228 (19)	0.2727 (3)	0.4609 (2)	0.0610 (6)
N1	0.56325 (18)	0.1339 (2)	0.64913 (17)	0.0411 (5)
N2	0.65614 (19)	0.0963 (2)	0.72163 (18)	0.0447 (5)
C6	0.3631 (2)	0.1080 (3)	0.5859 (2)	0.0434 (5)
C7	0.4625 (2)	0.0705 (3)	0.6613 (2)	0.0437 (6)
C1	0.3700 (2)	0.2072 (3)	0.4911 (2)	0.0444 (6)
C8	0.6446 (3)	−0.0200 (3)	0.8097 (2)	0.0582 (7)
H8A	0.5658	−0.0592	0.8067	0.087*
H8B	0.6609	0.0221	0.8852	0.087*
H8C	0.6994	−0.0995	0.7952	0.087*
C5	0.2542 (2)	0.0437 (4)	0.6081 (3)	0.0591 (7)
H5	0.2485	−0.024	0.6692	0.071*
C9	0.7587 (2)	0.1735 (3)	0.7057 (2)	0.0449 (6)
C2	0.2700 (3)	0.2389 (4)	0.4249 (3)	0.0578 (7)

H2	0.2745	0.3047	0.3624	0.069*
C3	0.1633 (3)	0.1742 (4)	0.4505 (3)	0.0681 (9)
H3	0.0966	0.1964	0.4052	0.082*
C10	0.8904 (3)	0.3907 (4)	0.5977 (3)	0.0668 (8)
H10A	0.8935	0.469	0.5405	0.1*
H10B	0.9466	0.3141	0.5798	0.1*
H10C	0.9087	0.4316	0.6732	0.1*
C4	0.1553 (3)	0.0767 (4)	0.5430 (3)	0.0725 (9)
H4	0.0833	0.0339	0.561	0.087*
H7	0.444 (3)	0.007 (4)	0.717 (3)	0.082 (11)*
H1O	0.527 (4)	0.253 (5)	0.518 (4)	0.087 (12)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0478 (4)	0.0548 (4)	0.0548 (4)	−0.0099 (3)	−0.0043 (3)	0.0076 (3)
S1	0.0517 (5)	0.0886 (6)	0.0702 (5)	0.0089 (4)	−0.0151 (4)	0.0073 (4)
O1	0.0498 (12)	0.0718 (13)	0.0614 (12)	−0.0079 (10)	0.0019 (10)	0.0231 (11)
N1	0.0439 (11)	0.0376 (10)	0.0420 (10)	0.0021 (8)	0.0009 (8)	0.0019 (8)
N2	0.0446 (11)	0.0443 (11)	0.0449 (11)	0.0052 (9)	−0.0033 (9)	0.0064 (9)
C6	0.0461 (13)	0.0399 (12)	0.0444 (12)	−0.0027 (10)	0.0045 (10)	−0.0078 (10)
C7	0.0509 (14)	0.0382 (12)	0.0424 (13)	−0.0036 (10)	0.0073 (10)	0.0003 (10)
C1	0.0461 (14)	0.0414 (12)	0.0458 (13)	0.0007 (10)	0.0044 (10)	−0.0043 (10)
C8	0.0687 (19)	0.0524 (15)	0.0535 (15)	0.0052 (13)	0.0018 (13)	0.0158 (12)
C5	0.0512 (16)	0.0632 (18)	0.0629 (17)	−0.0167 (13)	0.0031 (13)	0.0018 (14)
C9	0.0455 (14)	0.0455 (13)	0.0438 (13)	0.0070 (10)	0.0016 (10)	−0.0048 (10)
C2	0.0597 (17)	0.0575 (16)	0.0558 (16)	0.0069 (13)	−0.0035 (13)	−0.0027 (13)
C3	0.0525 (18)	0.079 (2)	0.072 (2)	0.0066 (15)	−0.0142 (15)	−0.0106 (17)
C10	0.0519 (17)	0.076 (2)	0.073 (2)	−0.0139 (15)	0.0075 (15)	0.0017 (16)
C4	0.0472 (17)	0.088 (2)	0.083 (2)	−0.0162 (16)	−0.0050 (15)	−0.0018 (19)

Geometric parameters ($\text{\AA}$, $^\circ$)

S2—C9	1.754 (3)	C8—H8A	0.96
S2—C10	1.796 (3)	C8—H8B	0.96
S1—C9	1.639 (3)	C8—H8C	0.96
O1—C1	1.353 (3)	C5—C4	1.366 (5)
O1—H1O	0.91 (4)	C5—H5	0.93
N1—C7	1.286 (3)	C2—C3	1.380 (5)
N1—N2	1.370 (3)	C2—H2	0.93
N2—C9	1.368 (3)	C3—C4	1.378 (5)
N2—C8	1.457 (3)	C3—H3	0.93
C6—C5	1.392 (4)	C10—H10A	0.96
C6—C1	1.408 (4)	C10—H10B	0.96
C6—C7	1.446 (4)	C10—H10C	0.96
C7—H7	0.89 (4)	C4—H4	0.93
C1—C2	1.381 (4)		

C9—S2—C10	102.00 (15)	C4—C5—C6	122.2 (3)
C1—O1—H1O	108 (3)	C4—C5—H5	118.9
C7—N1—N2	120.0 (2)	C6—C5—H5	118.9
C9—N2—N1	116.2 (2)	N2—C9—S1	123.3 (2)
C9—N2—C8	122.8 (2)	N2—C9—S2	112.69 (19)
N1—N2—C8	121.0 (2)	S1—C9—S2	124.01 (17)
C5—C6—C1	117.8 (3)	C3—C2—C1	120.8 (3)
C5—C6—C7	118.7 (2)	C3—C2—H2	119.6
C1—C6—C7	123.5 (2)	C1—C2—H2	119.6
N1—C7—C6	121.1 (2)	C4—C3—C2	120.2 (3)
N1—C7—H7	126 (2)	C4—C3—H3	119.9
C6—C7—H7	113 (2)	C2—C3—H3	119.9
O1—C1—C2	118.1 (3)	S2—C10—H10A	109.5
O1—C1—C6	122.3 (2)	S2—C10—H10B	109.5
C2—C1—C6	119.7 (3)	H10A—C10—H10B	109.5
N2—C8—H8A	109.5	S2—C10—H10C	109.5
N2—C8—H8B	109.5	H10A—C10—H10C	109.5
H8A—C8—H8B	109.5	H10B—C10—H10C	109.5
N2—C8—H8C	109.5	C5—C4—C3	119.4 (3)
H8A—C8—H8C	109.5	C5—C4—H4	120.3
H8B—C8—H8C	109.5	C3—C4—H4	120.3

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1O $\cdots$ S2	0.91 (5)	2.67 (5)	3.453 (2)	145 (4)
O1—H1O $\cdots$ N1	0.91 (5)	1.88 (5)	2.678 (3)	145 (4)