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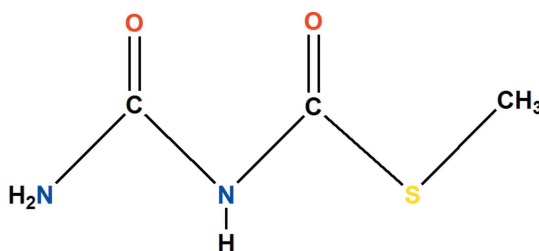
Crystal structure of *N*-[(methylsulfonyl)carbonyl]- urea

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The almost planar (r.m.s. deviation = 0.055 Å) title compound, (MeS)C(O)NH-C(O)NH₂, was formed during an attempted crystallization of dimethyl cyanocarbonimidodithioate with CrO₂Cl₂; an unexpected redox reaction converted the cyanocarbonimido moiety to a urea group and removed one methylthiol group. In the crystal, hydrogen-bonding interactions from the amide and amido N–H groups to carbonyl O atoms of neighbouring molecules result in [010] ribbon-like chains.

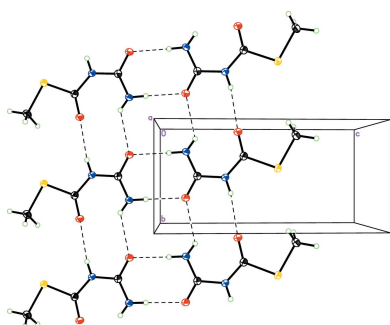
1. Chemical context

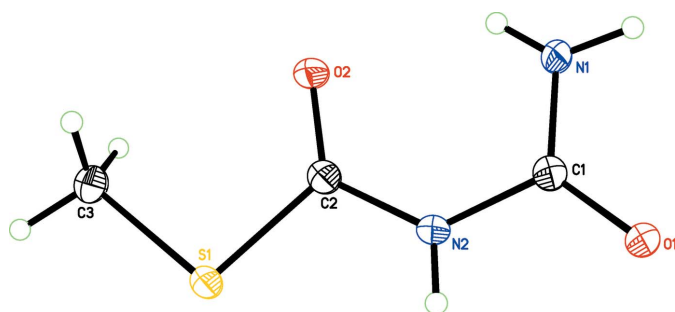
We have recently reported that dimethyl cyanocarbonimidodithioate (MeS)₂C=N–C≡N is an N-donor ligand, coordinating to metal centres (Diop *et al.*, 2016). In an attempt to broaden data on the coordination ability of this ligand, we have initiated here a study of the interactions between dimethyl cyanocarbonimidodithioate and CrO₂Cl₂ which yielded the title compound whose X-ray study is reported in this work. Surprisingly, the dimethyl cyanocarbonimidodithioate has undergone redox reactivity at both the cyanide (N1/C1) and the imido (N2/C2) functionalities. The carbon atoms associated with these groups have been oxidized to an amide and both nitrogen atoms now sport hydrogen atoms. One methylthiol group has been removed during this reaction. Presumably adventitious water is the source of the oxygen and hydrogen. This was unexpected reactivity. It is not known if or how the CrO₂Cl₂ plays a role in this reaction.



2. Structural commentary

The starting dimethyl cyanocarbonimidodithioate (MeS)₂C=N–C≡N has undergone oxidation yielding the title compound (MeS)C(O)NHC(O)NH₂ (Fig. 1). Bond distances and angles within the molecule are in the expected range (Sow *et al.*, 2014; Jalový *et al.*, 2011). Although the C1–N1 [1.3159 (19) Å] bond appears shorter than the C2–N2



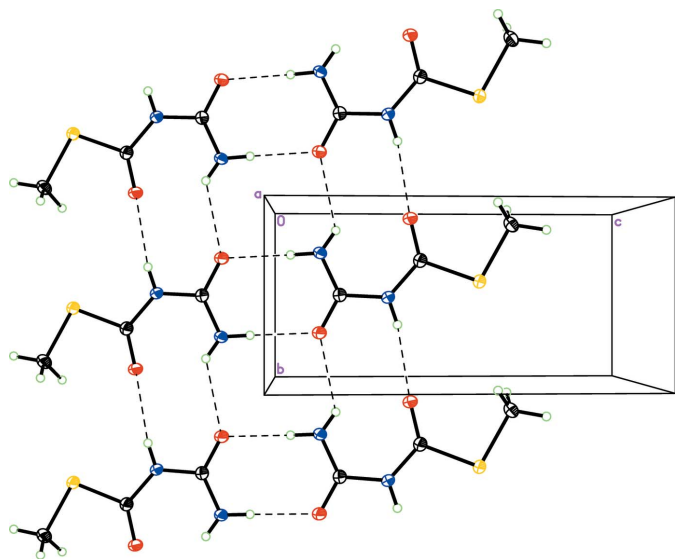

Figure 1

The molecular structure of the title compound. Displacement ellipsoids are depicted at the 50% probability level and H atoms as spheres of an arbitrary radius.

[1.3623 (18) Å] and C1–N2 [1.3977 (18) Å] bonds, all three are within expected ranges for urea N–C bond distances (*MOGUL* analysis; Bruno *et al.*, 2004) because of the different substituents on the carbon atoms. The C2–S1–C3 bond angle is 99.22 (7)°. The torsion angles are close to zero or 180°, which is consistent with a nearly planar molecule (r.m.s. deviation for the non-hydrogen atoms = 0.055 Å). An intramolecular N1–H1NB···O2 hydrogen bond generates an *S*(6) ring (see Table 1).

3. Supramolecular features

In the crystal, the compound forms a hydrogen-bonded dimer with a molecule related through the inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$ [N1···O1ⁱⁱ; symmetry code: (ii) $-x + 1, -y + 1, -z$]. This ‘head-to-head’ arrangement forces the non-interacting thio-methyl groups to be on the exterior of the chain. These hydrogen-bonded dimers propagate into a one-dimensional


Figure 2

Packing diagram of the title compound showing one-dimensional hydrogen-bonded chains (dashed lines) viewed along the *a* axis.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1NB···O1 ⁱ	0.77 (2)	2.27 (2)	2.8518 (16)	132.3 (19)
N1–H1NB···O2	0.77 (2)	2.15 (2)	2.7397 (17)	134 (2)
N1–H1NA···O1 ⁱⁱⁱ	0.87 (2)	2.05 (2)	2.9221 (16)	178 (2)
N2–H2NA···O2 ⁱⁱⁱ	0.805 (19)	2.18 (2)	2.9709 (15)	168.9 (16)
C3–H3A···O2 ^{iv}	0.98	2.54	3.494 (2)	166
C3–H3B···S1 ^v	0.98	2.85	3.7064 (15)	147

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 1, -y + 1, -z$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y, -z + 1$; (v) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

chain parallel to the *b* axis (Fig. 2) through hydrogen bonds from N1···O1ⁱ and N2···O2ⁱⁱⁱ [symmetry codes: (i) $x, y - 1, z$; (iii) $x, y + 1, z$]. The ribbons are oriented approximately parallel to the $[30\bar{1}]$ plane. The compactness and the stability of the structure are consolidated through van der Waals forces and weak C–H···O and C–H···S hydrogen bonds (Table 1).

4. Database survey

To the best of our knowledge there are no reported structures that contain the *N*-[(methylsulfanyl)carbonyl]urea group (CSD Version 5.37 plus one update; Groom & Allen, 2014).

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₃ H ₆ N ₂ O ₂ S
<i>M_r</i>	134.16
Crystal system, space group	Monoclinic, <i>P</i> ₂ /n
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9388 (13), 5.0999 (6), 10.6755 (14)
β (°)	94.136 (4)
<i>V</i> (Å ³)	539.70 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.50
Crystal size (mm)	0.24 × 0.19 × 0.14
Data collection	
Diffractometer	Bruker Kappa X8–APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.679, 0.734
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8437, 1344, 1220
<i>R_{int}</i>	0.024
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.669
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.031, 0.084, 1.09
No. of reflections	1344
No. of parameters	86
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.38, –0.23

Computer programs: *APEX3* (Bruker, 2015), *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

All chemicals are purchased from Aldrich Company (Germany) and used as received. Dimethyl cyanocarbonimidodithioate was mixed in acetonitrile with CrO_2Cl_2 in a 1:1 ratio: a green solution was obtained. Two colourless crystals – one of which being this studied compound – suitable for a single-crystal X-ray diffraction study were obtained after a slow solvent evaporation at room temperature (303 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Urea hydrogen atoms were located from a difference Fourier map and refined freely. Methyl hydrogen atoms were included in geometrically calculated positions and allowed to rotate to minimize their contribution to electron density with $\text{C-H} = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C3})$.

Acknowledgements

The authors acknowledge the Cheikh Anta Diop University of Dakar (Sénégal) and the University of Notre Dame (USA) for

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Crystal structure of *N*-[(methylsulfanyl)carbonyl]urea

Mouhamadou Birame Diop, Libasse Diop and Allen G. Oliver

Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

N-[(Methylsulfanyl)carbonyl]urea

Crystal data

$C_3H_6N_2O_2S$

$M_r = 134.16$

Monoclinic, $P2_1/n$

$a = 9.9388$ (13) Å

$b = 5.0999$ (6) Å

$c = 10.6755$ (14) Å

$\beta = 94.136$ (4)°

$V = 539.70$ (12) Å³

$Z = 4$

$F(000) = 280$

$D_x = 1.651$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3996 reflections

$\theta = 2.7$ – 28.3 °

$\mu = 0.50$ mm⁻¹

$T = 120$ K

Tablet, colorless

$0.24 \times 0.19 \times 0.14$ mm

Data collection

Bruker Kappa X8-APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

combination of ω and φ -scans

Absorption correction: multi-scan
(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.679$, $T_{\max} = 0.734$

8437 measured reflections

1344 independent reflections

1220 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 2.7$ °

$h = -13 \rightarrow 13$

$k = -6 \rightarrow 6$

$l = -8 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.084$

$S = 1.09$

1344 reflections

86 parameters

0 restraints

Primary atom site location: real-space vector
search

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.2127P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.38$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻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.

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	0.69406 (4)	0.42571 (7)	0.54507 (3)	0.01914 (14)
O1	0.54686 (11)	0.7074 (2)	0.13127 (9)	0.0204 (2)
O2	0.62689 (10)	0.08127 (18)	0.36859 (10)	0.0183 (2)
N1	0.55218 (13)	0.2665 (2)	0.13289 (12)	0.0186 (3)
H1NB	0.5637 (18)	0.144 (5)	0.1744 (19)	0.025 (5)*
H1NA	0.521 (2)	0.276 (5)	0.055 (2)	0.036 (5)*
N2	0.61955 (13)	0.5113 (2)	0.31095 (12)	0.0162 (3)
H2NA	0.6285 (16)	0.660 (4)	0.3351 (16)	0.013 (4)*
C1	0.57029 (14)	0.4988 (3)	0.18511 (13)	0.0157 (3)
C2	0.64159 (13)	0.3108 (3)	0.39424 (12)	0.0154 (3)
C3	0.70883 (16)	0.1190 (3)	0.62609 (14)	0.0229 (3)
H3A	0.6205	0.0327	0.6228	0.034*
H3B	0.7408	0.1494	0.7139	0.034*
H3C	0.7732	0.0067	0.5860	0.034*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0303 (2)	0.0137 (2)	0.0128 (2)	−0.00005 (12)	−0.00299 (14)	−0.00060 (12)
O1	0.0322 (6)	0.0120 (5)	0.0162 (5)	0.0004 (4)	−0.0045 (4)	0.0002 (4)
O2	0.0258 (5)	0.0117 (5)	0.0169 (5)	−0.0011 (4)	−0.0023 (4)	−0.0009 (4)
N1	0.0296 (7)	0.0110 (6)	0.0143 (6)	0.0009 (5)	−0.0044 (5)	0.0012 (5)
N2	0.0234 (6)	0.0112 (6)	0.0137 (6)	−0.0014 (4)	−0.0009 (4)	−0.0014 (4)
C1	0.0182 (6)	0.0146 (6)	0.0141 (6)	0.0002 (5)	0.0003 (5)	0.0000 (5)
C2	0.0165 (6)	0.0153 (6)	0.0143 (6)	−0.0001 (5)	0.0000 (5)	−0.0006 (5)
C3	0.0336 (8)	0.0172 (7)	0.0170 (7)	−0.0016 (6)	−0.0037 (6)	0.0041 (5)

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

S1—C2	1.7569 (14)	C2—N2	1.3623 (18)
S1—C3	1.7885 (15)	C1—N2	1.3977 (18)
C1—O1	1.2239 (18)	N2—H2NA	0.805 (19)
C2—O2	1.2088 (17)	C3—H3A	0.9800
C1—N1	1.3159 (19)	C3—H3B	0.9800
N1—H1NB	0.77 (2)	C3—H3C	0.9800
N1—H1NA	0.87 (2)		
C2—S1—C3	99.22 (7)	O2—C2—N2	124.61 (13)
C1—N1—H1NB	118.6 (16)	O2—C2—S1	123.61 (11)

C1—N1—H1NA	112.5 (16)	N2—C2—S1	111.78 (10)
H1NB—N1—H1NA	129 (2)	S1—C3—H3A	109.5
C2—N2—C1	128.44 (12)	S1—C3—H3B	109.5
C2—N2—H2NA	119.3 (12)	H3A—C3—H3B	109.5
C1—N2—H2NA	112.0 (12)	S1—C3—H3C	109.5
O1—C1—N1	124.62 (13)	H3A—C3—H3C	109.5
O1—C1—N2	116.95 (13)	H3B—C3—H3C	109.5
N1—C1—N2	118.43 (13)		
C2—N2—C1—O1	173.40 (14)	C1—N2—C2—S1	-176.11 (11)
C2—N2—C1—N1	-6.5 (2)	C3—S1—C2—O2	-1.02 (14)
C1—N2—C2—O2	3.7 (2)	C3—S1—C2—N2	178.83 (11)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1NB...O1 ⁱ	0.77 (2)	2.27 (2)	2.8518 (16)	132.3 (19)
N1—H1NB...O2	0.77 (2)	2.15 (2)	2.7397 (17)	134 (2)
N1—H1NA...O1 ⁱⁱ	0.87 (2)	2.05 (2)	2.9221 (16)	178 (2)
N2—H2NA...O2 ⁱⁱⁱ	0.805 (19)	2.18 (2)	2.9709 (15)	168.9 (16)
C3—H3A...O2 ^{iv}	0.98	2.54	3.494 (2)	166
C3—H3B...S1 ^v	0.98	2.85	3.7064 (15)	147

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, -z$; (iii) $x, y+1, z$; (iv) $-x+1, -y, -z+1$; (v) $-x+3/2, y-1/2, -z+3/2$.