organic papers

# S,S'-Bis(methoxycarbonylmethyl)dithioglyoxime monohydrate

Serkan Soylu,[a]* Mehmet Kandaz[b] and Nezihe Çalışkan[a]

[a]Ondokuz Mayıs University, Arts and Sciences Faculty, Department of Physics, 55139 Samsun, Turkey, and [b]University of Sakarya, Arts and Sciences Faculty, Department of Chemistry, 54100 Mithatpaşa/Sakarya, Turkey

Correspondence e-mail: mssoylu@omu.edu.tr

The title compound, dimethyl [1,2-bis(hydroxyimino)ethane-1,2-diyl]dithiodiacetate monohydrate, $C_8H_{12}N_2O_6S_2 \cdot H_2O$, consists of a polymeric arrangement of molecules linked through O—H···OW and OW—HW···O hydrogen bonds. All these hydrogen-bond interactions result in the formation of infinite layers parallel to the (110) plane. The oxime group has an E configuration. The molecule has a twofold axis passing through the mid-point of the central C—C bond. The water molecule is also located on a twofold axis.

Comment

The coordination chemistry of *vic*-dioximes is interesting and numerous transition metal complexes of these ligands have been investigated. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structures, stabilized by hydrogen bonding (Schrauzer & Kohnle, 1964). The high stability of complexes prepared with *vic*-dioxime ligands has been used extensively for various purposes. For example, some of these complexes may possess the properties of semiconductors (Schrauzer & Windgassen, 1967) or show high conductivity (Kobayashi *et al.*, 1993). Apart from these properties, oxime (—C=N—OH) groups possess stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman *et al.*, 1999). The configurational and conformational isomers of glyoxime derivatives (dioximes) have been analyzed (Chertanova *et al.*, 1994).

(I)
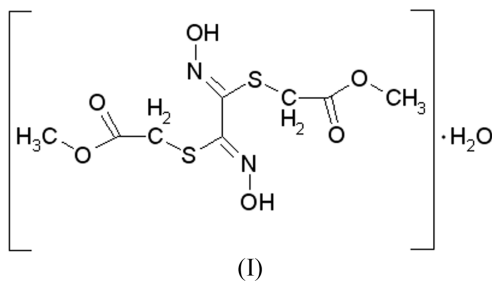
The crystal structure determination of the title molecule, (I), was carried out in order to understand the strength of the hydrogen-bonding capabilities of oxime groups having classical —C=N—OH structures. As shown in Fig. 1, the title compound, (I), consists of two glyoxime (C=N—OH) moieties and two mercaptoacetic acid methyl ester ($C_3H_5O_2S$) groups. The molecule is arranged around a twofold axis passing through the mid-point of C1—C1[i] [C1—C1[i] = 1.483 (4) Å; symmetry code: (i) $-x, y, \frac{1}{2} - z$]. Furthermore, water molecules located on twofold axes are present in the
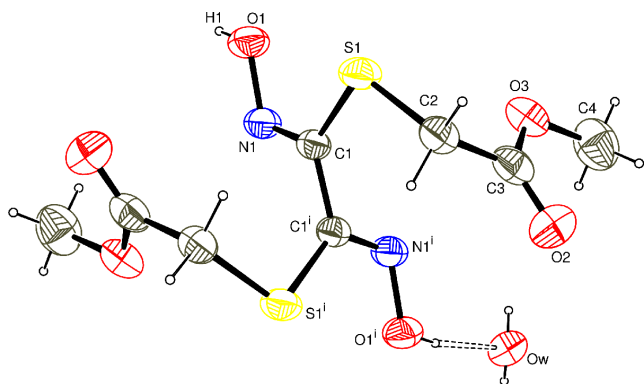
Figure 1
ORTEP-3 drawing (Farrugia, 1997) of the molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

crystal structure. The glyoxime planes (O1/N1/C1 and O1^i/N1^i/C1^i) are nearly perpendicular, as shown by the dihedral angle of 89.8 (3)°.

In the title compound, (I), the glyoxime moiety has an *E* configuration, with a C1^i—C1—N1—O1 torsion angle of 179.2°(2). In this configuration, atom O1 of the oxime group behaves as donor and atom O2 of the carboxyl group behaves as acceptor with respect to the water molecules, forming a two-dimensional hydrogen-bond network (Table 2). As can be seen from the packing diagram (Fig. 2), the layer resulting from the hydrogen-bonding interactions is nearly parallel to the (110) plane. The crystal structure is built up from parallel layers related by inversion centres, with no hydrogen-bonding interactions between them (Fig. 2).

Experimental

2-Methylthioglycolate (0.674 g, 6.36 mmol) was dissolved in dry tetrahydrofuran (THF, 50 ml) under nitrogen, and anhydrous NaHCO$_3$ (0.53 g, 36 mmol) was added, with stirring, at room temperature. To this solution, (*E,E*)-dichloroglyoxime (0.5 g, 3.18 mmol) in dry THF (25 ml) was added dropwise over a period of 0.5 h and the solution was stirred at room temperature overnight. The colour of the solution turned light yellow during the course of the reaction. The reaction mixture was then stirred at 308 K for an additional 4 h. After that, the mixture was allowed to cool to room temperature and the NaCl formed during the reaction was filtered off. The volume of the reaction mixture was reduced to 15–20 ml and the yellow solution was taken up in a chloroform phase. The excess of mercapto starting material was removed by washing the solution with NaHCO$_3$ (5%). The organic phase was washed with water and dried over Na$_2$SO$_4$. After filtration on a drying agent, the filtrate was evaporated to dryness. The title compound separated as white crystals and these were dried *in vacuo* at room temperature (yield 0.83 g, 88.17%; m.p.: 340 K). This compound is soluble in CHCl$_3$, CH$_2$Cl$_2$, THF, dimethylformamide and dimethyl sulfoxide. IR (KBr, thin film): ν 3040 (aromatic H), 2964 (aliphatic H), 2923–2850 (aliphatic H), 1723 (COOR), 1618 (C=N), 1585 (NH), 1456, 1391 (aromatic skeleton vibration), 1310–1274, 1209, 1005 (N—O), 893, 747 (strong), 654, 618, 545, 446, 435. ^{1}H NMR (250 MHz, DMSO-d_6): δ 12.16 (*s*, 2H, =N-OH, *D*-exchangeable), 3.73 (*s*, 4H, –SCH$_2$COO*R*), 3.64 (*s*, 6H, –CH$_3$–OOC); UV–vis (in DMSO) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 3304 (*sh*), 285 (*sh*), 258 (12.83); MS (EI): *m/z* = 296 (100) [*M*$^+$], 318 (35)
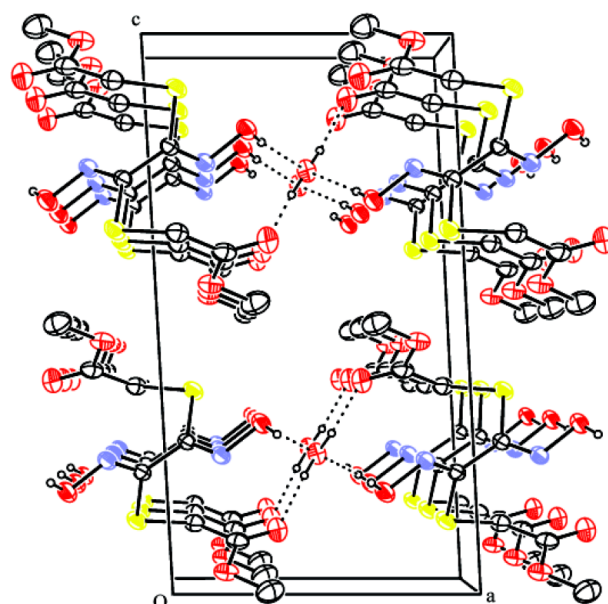

Figure 2
Packing view, showing the layer formed by the O—H···O interactions (dashed lines). Displacement ellipsoids are drawn at the 30% probability level.

[*M* + Na]$^+$, 279.2 (10) [*M* − H$_2$O]$^+$, 231.95 (25) [*M* − 2 CH$_3$OH]$^+$, 156.94 (100) [DCGO]$^+$.

Crystal data

C$_8$H$_{12}$N$_2$O$_6$S$_2$·H$_2$O	$D_x = 1.470$ Mg m^{-3}
$M_r = 314.33$	Mo $K\alpha$ radiation
Monoclinic, $P2/c$	Cell parameters from 2904
$a = 8.6173$ (15) Å	reflections
$b = 5.2953$ (7) Å	$\theta = 2.4–26.5°$
$c = 15.588$ (3) Å	$\mu = 0.40$ mm^{-1}
$\beta = 93.214$ (14)°	$T = 293$ (2) K
$V = 710.2$ (2) Å^3	Prosm, colourless
$Z = 2$	$0.31 \times 0.26 \times 0.20$ mm

Data collection

Stoe IPDS-2 diffractometer	1255 independent reflections
φ scans	895 reflections with $I > 2\sigma(I)$
Absorption correction: by	$R_{int} = 0.076$
integration (*X-RED*32;	$\theta_{max} = 25.0°$
Stoe & Cie, 2002)	$h = -10 \rightarrow 9$
$T_{min} = 0.900$, $T_{max} = 0.941$	$k = -6 \rightarrow 6$
4196 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.058$	independent and constrained
$wR(F^2) = 0.157$	refinement
$S = 0.93$	$w = 1/[\sigma^2(F_o^2) + (0.1116P)^2]$
1255 reflections	where $P = (F_o^2 + 2F_c^2)/3$
92 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.49$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.751 (3)	N1—C1	1.271 (4)
S1—C2	1.787 (4)	N1—O1	1.393 (3)
C1—S1—C2	102.81 (15)	N1—C1—C1^i	116.6 (2)
C1—N1—O1	110.8 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$\cdots$OW	0.82	1.89	2.706 (4)	170
OW—HW1$\cdots$O2^{ii}	0.83 (4)	1.96 (2)	2.765 (4)	163 (4)

Symmetry code: (ii) $-x, y - 1, \frac{1}{2} - z$.

H atoms attached to C atoms and to the hydroxyl atom O1 were introduced in calculated positions and treated as riding on their parent atoms, with O—H = 0.82 Å and C—H = 0.96–0.97 Å. The H atoms of the water molecule were located in a difference map and no restraints were applied. $U_{iso}(H)$ values were constrained to be $1.5U_{eq}$ of the carrier atom for CH_3, and $1.2U_{eq}$ for CH_2 and OH or OH_2.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

References

Chertanova, L., Pascard, C. & Sheremetev, A. (1994). *Acta Cryst.* B**50**, 708–716.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kobayashi, N., Andrew, W., Mizunuma, N. S., Awaji, H. & Tamaguchi, M. (1993). *Chem. Phys. Lett.* **205**, 51–54.
Marsman, A. W., Leussing, E. D., Zwikker, J. W. & Jenneskens, L. W. (1999). *Chem. Mater.* **11**, 1484–1491.
Schrauzer, G. N. & Kohnle, J. (1964). *Chem. Ber.* **97**, 3056–3063.
Schrauzer, G. N. & Windgassen, J. (1967). *J. Am. Chem. Soc.* **89**, 143–146.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.