organic compounds

4-(4-Oxopent-2-en-2-ylamino)-1,2,4-triazol-1-ium-5-thiolate

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In the title compound, $C_8H_{12}N_4OS$, an intramolecular N—H···O hydrogen bond links the imine N atom to the oxo O atom. In the crystal, molecules are linked by intermolecular N—H···O and N—H···S hydrogen bonds, forming a two-dimensional framework.

Related literature

For Schiff base metal complexes, see: Lacroix (2001); Sabater *et al.* (2001). For the use of 1,2,4-triazole and its derivatives as ligands to bridge metal ions, see: Yi *et al.* (2004).
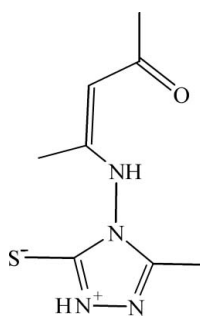
Experimental

Crystal data

$C_8H_{12}N_4OS$	Monoclinic, $P2_1/n$
$M_r = 212.28$	$a = 10.620$ (6) Å
$b = 9.520$ (5) Å	Mo $K\alpha$ radiation
$c = 10.764$ (5) Å	$\mu = 0.28$ mm^{-1}
$\beta = 99.560$ (14)°	$T = 293$ K
$V = 1073.2$ (10) Å^3	$0.26 \times 0.23 \times 0.18$ mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	9199 measured reflections
	2071 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	1688 reflections with $I > 2\sigma(I)$
$T_{min} = 0.932$, $T_{max} = 0.952$	$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	130 parameters
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
2071 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.03	2.659 (2)	130
N1—H1···S1^i	0.86	2.81	3.4127 (19)	129
N3—H3A···O1^{ii}	0.86	1.93	2.772 (2)	166

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

4-(4-Oxopent-2-en-2-ylamino)-1,2,4-triazol-1-ium-5-thiolate

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S1. Comment

Schiff base metal complexes have been widely investigated for their properties and applications in different fields, catalysis (Sabater *et al.*, 2001), materials chemistry (Lacroix 2001) and simple organic molecules, such as 1,2,4-triazole and its derivatives, which usually studied as precursors of compounds with importance in medicine biology and industry, have gained more and more interest as ligands to bridge metal ions due to their potential bridging fashions (Yi *et al.*, 2004). In this work, we report a crystal structure of 3-methyl-4-amino-5-mercapto-1,2,4- triazole, (I).

The crystal structure of the title compound is shown in Fig. 1. The molecule is a non-coplanar structure, an intramolecular N1—H1···O1 hydrogen bonds linking the amines N1 atoms to the enolic O1 atoms. As shown in Fig. 2, the molecules of the title compound are lined up by the intermolecular N1—H1···S1 and N3—H3A···O1 interactions (Table 2) forming a two-dimensional framework.

S2. Experimental

Acetylacetone (1.0 g, 10 mmol) was added to an ethanol solution containing 3-methyl-4-amino-5-mercapto-1,2,4-triazole (1.3 g, 10 mmol). The mixture was heated, stirring for 24 h. The yellow residue yielded and was removed from the solution by filtration, washing with ethanol 3 times, 1.47 g, in a yield of 69%. Single crystals suitable for X-ray diffraction were obtained from an ethanol-CH_2Cl_2 mixture (1:1, v:v) by slow evaporation at room temperature.

S3. Refinement

All H atoms were placed in calculated positions and refined as riding, with C—H = 0.93–0.96 Å, N—H = 0.8600 Å, and $U_{iso}(H) = 1.2$–$1.5U_{eq}(C, N)$.
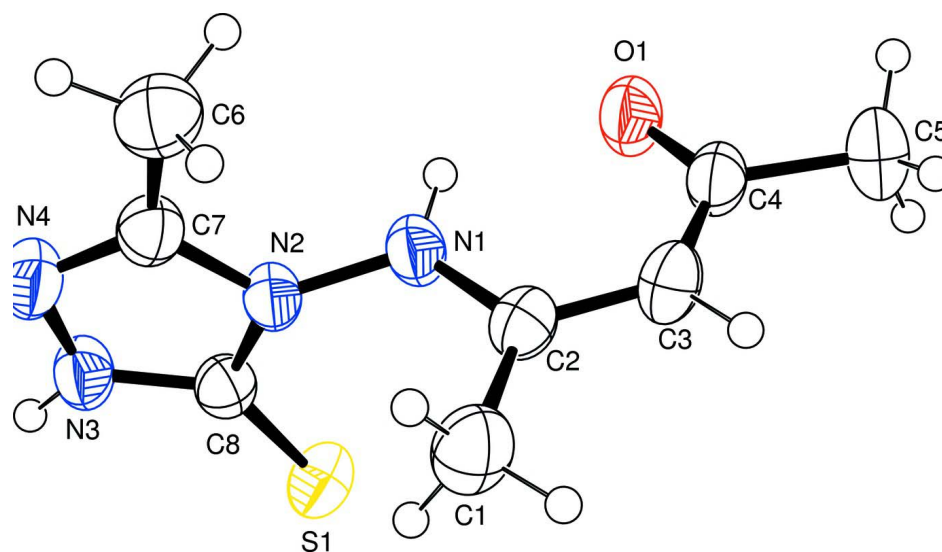
Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

4-(4-Oxopent-2-en-2-ylamino)-1,2,4-triazol-1-ium-5-thiolate

Crystal data

$C_8H_{12}N_4OS$	$F(000) = 448$
$M_r = 212.28$	$D_x = 1.314$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 9199 reflections
$a = 10.620$ (6) Å	$\theta = 2.5–26.0°$
$b = 9.520$ (5) Å	$\mu = 0.28$ mm^{-1}
$c = 10.764$ (5) Å	$T = 293$ K
$\beta = 99.560$ (14)°	Prism, yellow
$V = 1073.2$ (10) Å^3	$0.26 \times 0.23 \times 0.18$ mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	9199 measured reflections
Radiation source: fine-focus sealed tube	2071 independent reflections
Graphite monochromator	1688 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan	$\theta_{max} = 26.0°$, $\theta_{min} = 2.5°$
(*SADABS*; Bruker, 2005)	$h = -12\rightarrow13$
$T_{min} = 0.932$, $T_{max} = 0.952$	$k = -11\rightarrow11$
	$l = -13\rightarrow13$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.038$	
$wR(F^2) = 0.105$	Secondary atom site location: difference Fourier map
$S = 1.06$	
2071 reflections	Hydrogen site location: inferred from neighbouring sites
130 parameters	

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.3337P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.24$ e Å^{-3}

$\Delta\rho_{min} = -0.22$ e Å^{-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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.6978 (2)	0.4476 (2)	0.6177 (2)	0.0581 (6)
H1A	0.6385	0.4804	0.6695	0.087*
H1B	0.7230	0.5246	0.5697	0.087*
H1C	0.7717	0.4092	0.6702	0.087*
C2	0.63580 (17)	0.3365 (2)	0.53014 (16)	0.0413 (4)
C3	0.51805 (18)	0.2824 (2)	0.53712 (17)	0.0474 (5)
H3	0.4781	0.3133	0.6027	0.057*
C4	0.45166 (17)	0.1828 (2)	0.45229 (17)	0.0437 (4)
C5	0.31956 (19)	0.1390 (3)	0.4704 (2)	0.0598 (6)
H5A	0.2574	0.1966	0.4191	0.090*
H5B	0.3113	0.1500	0.5573	0.090*
H5C	0.3058	0.0423	0.4464	0.090*
C6	0.9660 (2)	0.1873 (2)	0.5572 (2)	0.0579 (5)
H6A	1.0551	0.1644	0.5677	0.087*
H6B	0.9162	0.1048	0.5318	0.087*
H6C	0.9457	0.2212	0.6355	0.087*
C7	0.93642 (17)	0.29676 (19)	0.45994 (16)	0.0420 (4)
C8	0.81958 (17)	0.45095 (18)	0.33090 (15)	0.0377 (4)
N1	0.70361 (13)	0.28695 (16)	0.44362 (13)	0.0430 (4)
H1	0.6761	0.2136	0.4010	0.052*
N2	0.81498 (13)	0.34888 (15)	0.42069 (13)	0.0381 (3)
N3	0.94393 (14)	0.45391 (16)	0.32250 (14)	0.0445 (4)
H3A	0.9753	0.5092	0.2723	0.053*
N4	1.01765 (14)	0.35996 (17)	0.40183 (15)	0.0483 (4)
O1	0.49708 (12)	0.13376 (15)	0.36199 (13)	0.0536 (4)
S1	0.69902 (5)	0.54628 (5)	0.25545 (4)	0.04948 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0537 (13)	0.0681 (14)	0.0536 (11)	−0.0014 (10)	0.0118 (10)	−0.0165 (10)
C2	0.0402 (10)	0.0460 (10)	0.0389 (9)	0.0044 (8)	0.0103 (8)	0.0013 (7)

C3	0.0418 (11)	0.0602 (12)	0.0439 (10)	0.0030 (9)	0.0180 (8)	−0.0033 (9)
C4	0.0370 (10)	0.0495 (11)	0.0474 (10)	0.0029 (8)	0.0151 (8)	0.0062 (8)
C5	0.0426 (12)	0.0754 (15)	0.0653 (13)	−0.0085 (10)	0.0198 (10)	0.0014 (11)
C6	0.0566 (13)	0.0560 (12)	0.0597 (12)	0.0071 (10)	0.0055 (10)	0.0110 (10)
C7	0.0369 (10)	0.0440 (10)	0.0447 (9)	0.0003 (8)	0.0055 (8)	−0.0035 (8)
C8	0.0379 (10)	0.0402 (9)	0.0360 (8)	−0.0018 (7)	0.0089 (7)	−0.0040 (7)
N1	0.0388 (9)	0.0446 (9)	0.0490 (8)	−0.0086 (7)	0.0175 (7)	−0.0082 (7)
N2	0.0316 (8)	0.0411 (8)	0.0427 (8)	−0.0030 (6)	0.0092 (6)	−0.0012 (6)
N3	0.0359 (9)	0.0500 (9)	0.0493 (9)	−0.0028 (7)	0.0116 (7)	0.0062 (7)
N4	0.0339 (8)	0.0570 (10)	0.0536 (9)	0.0008 (7)	0.0059 (7)	0.0037 (7)
O1	0.0461 (8)	0.0604 (9)	0.0591 (8)	−0.0084 (6)	0.0223 (7)	−0.0143 (7)
S1	0.0430 (3)	0.0588 (3)	0.0476 (3)	0.0104 (2)	0.0103 (2)	0.0053 (2)

Geometric parameters (Å, º)

C1—C2	1.495 (3)	C6—C7	1.474 (3)
C1—H1A	0.9600	C6—H6A	0.9600
C1—H1B	0.9600	C6—H6B	0.9600
C1—H1C	0.9600	C6—H6C	0.9600
C2—N1	1.353 (2)	C7—N4	1.295 (2)
C2—C3	1.366 (3)	C7—N2	1.381 (2)
C3—C4	1.420 (3)	C8—N3	1.339 (2)
C3—H3	0.9300	C8—N2	1.377 (2)
C4—O1	1.245 (2)	C8—S1	1.6664 (19)
C4—C5	1.507 (3)	N1—N2	1.380 (2)
C5—H5A	0.9600	N1—H1	0.8600
C5—H5B	0.9600	N3—N4	1.386 (2)
C5—H5C	0.9600	N3—H3A	0.8600
C2—C1—H1A	109.5	C7—C6—H6B	109.5
C2—C1—H1B	109.5	H6A—C6—H6B	109.5
H1A—C1—H1B	109.5	C7—C6—H6C	109.5
C2—C1—H1C	109.5	H6A—C6—H6C	109.5
H1A—C1—H1C	109.5	H6B—C6—H6C	109.5
H1B—C1—H1C	109.5	N4—C7—N2	110.40 (16)
N1—C2—C3	120.20 (17)	N4—C7—C6	126.26 (17)
N1—C2—C1	116.86 (17)	N2—C7—C6	123.32 (16)
C3—C2—C1	122.92 (17)	N3—C8—N2	102.27 (15)
C2—C3—C4	125.30 (16)	N3—C8—S1	129.95 (14)
C2—C3—H3	117.4	N2—C8—S1	127.77 (14)
C4—C3—H3	117.4	C2—N1—N2	122.95 (15)
O1—C4—C3	122.48 (17)	C2—N1—H1	118.5
O1—C4—C5	119.12 (18)	N2—N1—H1	118.5
C3—C4—C5	118.38 (17)	C8—N2—N1	123.94 (14)
C4—C5—H5A	109.5	C8—N2—C7	109.16 (14)
C4—C5—H5B	109.5	N1—N2—C7	125.19 (15)
H5A—C5—H5B	109.5	C8—N3—N4	114.05 (15)
C4—C5—H5C	109.5	C8—N3—H3A	123.0

H5A—C5—H5C	109.5	N4—N3—H3A	123.0
H5B—C5—H5C	109.5	C7—N4—N3	104.12 (15)
C7—C6—H6A	109.5		

N1—C2—C3—C4	−5.7 (3)	C2—N1—N2—C7	105.0 (2)
C1—C2—C3—C4	176.25 (19)	N4—C7—N2—C8	0.6 (2)
C2—C3—C4—O1	0.7 (3)	C6—C7—N2—C8	179.02 (17)
C2—C3—C4—C5	−177.3 (2)	N4—C7—N2—N1	166.12 (16)
C3—C2—N1—N2	171.33 (16)	C6—C7—N2—N1	−15.5 (3)
C1—C2—N1—N2	−10.5 (3)	N2—C8—N3—N4	−0.11 (19)
N3—C8—N2—N1	−166.02 (14)	S1—C8—N3—N4	179.01 (13)
S1—C8—N2—N1	14.8 (2)	N2—C7—N4—N3	−0.62 (19)
N3—C8—N2—C7	−0.27 (18)	C6—C7—N4—N3	−178.99 (18)
S1—C8—N2—C7	−179.42 (13)	C8—N3—N4—C7	0.5 (2)
C2—N1—N2—C8	−91.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.03	2.659 (2)	130
N1—H1···S1ⁱ	0.86	2.81	3.4127 (19)	129
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