

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

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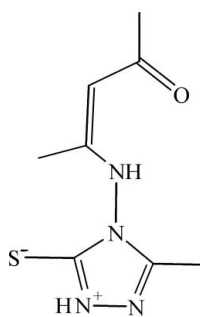
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.105; data-to-parameter ratio = 15.9.

In the title compound, $\text{C}_8\text{H}_{12}\text{N}_4\text{OS}$, an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond links the imine N atom to the oxo O atom. In the crystal, molecules are linked by intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{S}$ 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

$\text{C}_8\text{H}_{12}\text{N}_4\text{OS}$
 $M_r = 212.28$

Monoclinic, $P2_1/n$
 $a = 10.620$ (6) Å

$b = 9.520$ (5) Å
 $c = 10.764$ (5) Å
 $\beta = 99.560$ (14)°
 $V = 1073.2$ (10) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.28$ mm⁻¹
 $T = 293$ K
 $0.26 \times 0.23 \times 0.18$ mm

Data collection

Bruker SMART APEXII CCD
area-detector diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2005)
 $T_{\min} = 0.932$, $T_{\max} = 0.952$

9199 measured reflections
2071 independent reflections
1688 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.105$
 $S = 1.06$
2071 reflections

130 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

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

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

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

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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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2792).

References

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supplementary materials

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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 \cdots 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 \cdots S1 and N3—H3A \cdots O1 interactions (Table 2) forming a two-dimensional framework.

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-CH₂Cl₂ mixture (1:1, v:v) by slow evaporation at room temperature.

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 $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C}, \text{N})$.

Figures

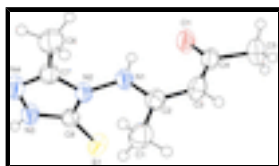


Fig. 1. The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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

Crystal data

C₈H₁₂N₄OS

$M_r = 212.28$

$F_{000} = 448$

$D_x = 1.314 \text{ Mg m}^{-3}$

supplementary materials

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.620$ (6) Å

$b = 9.520$ (5) Å

$c = 10.764$ (5) Å

$\beta = 99.560$ (14)°

$V = 1073.2$ (10) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 9199 reflections

$\theta = 2.5$ – 26.0 °

$\mu = 0.28$ mm⁻¹

$T = 293$ K

Prism, yellow

$0.26 \times 0.23 \times 0.18$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.932$, $T_{\max} = 0.952$

9199 measured reflections

2071 independent reflections

1688 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 26.0$ °

$\theta_{\min} = 2.5$ °

$h = -12 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.105$

$S = 1.06$

2071 reflections

130 parameters

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

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

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

Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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)

supplementary materials

Geometric parameters (Å, °)

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, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1	0.86	2.03	2.659 (2)	130
N1—H1 \cdots S1 ⁱ	0.86	2.81	3.4127 (19)	129
N3—H3A \cdots O1 ⁱⁱ	0.86	1.93	2.772 (2)	166

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Fig. 1

