Products of the oxidation of 1-(diaminomethylene)thiourea with hydrogen peroxide

Małgorzata Hołyńska* and Maria Kubiak

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50-383 Wrocław, Poland

Correspondence e-mail: holynska@wcheto.chem.uni.wroc.pl

Two oxidation products of 1-(diaminomethylene)thiourea (HATU) are reported, obtained from reactions with hydrogen peroxide at two different concentrations; these are 3,5-diamino-1,2,4-thiadiazole, $C_2H_4N_4S$, (I), related to HATU by intramolecular N—S bond formation, and 1-(diaminomethylene)uronium hydrogen sulfate, $C_2H_7N_4O^+\cdot HSO_4^-$, (II). In (I), molecular hydrogen-bonded chains could be distinguished, further organized in a herring-bone-like pattern. The structure of (II) is stabilized by an extensive network of N—H···O and O—H···O hydrogen bonds, where hydrogen-bonded anion chains and characteristic cation–anion motifs are present. The compounds are of importance not only with respect to crystal engineering, but also in the design of new synthetic routes to HATU transition metal complexes.

Comment

1-(Diaminomethylene)thiourea (HATU) is a derivative of biuret, in which one O atom has been notionally replaced by an S atom while the remaining amide group has been replaced by –CH(NH₂)₂. This simple molecule has attracted interest for its use as a starting compound to obtain so-called 'metalla-cages', e.g. [Ni₆(ATU)₈Cl](ClO₄)₃ (where ATU is the deprotonated form of HATU; Diaz et al., 2004; Gale & Quesada, 2006; Gimeno & Vilar, 2006; Lankshear & Beer, 2006). Such compounds are formed only in the presence of chloride ions, so that the reaction could serve as a method of colorimetric chloride detection. HATU has also been used as a component of resins chelating such ions as Ag⁺ (Trochimczuk & Kolarz, 2000). The reported transition metal complexes containing HATU as a ligand with known structure include the complexes with Ni (Kabir et al., 2002; Vilar et al., 1998, 1999; Diaz et al., 2004), Pd (Chakrabarty et al., 1990; Doxiadi et al., 2003), Ni and Pd (Cheng et al., 2001; Vilar et al., 1999; Doxiadi et al., 2003). Metal complexes with HATU of so far unknown structure include the nitrosyl complexes with Co, Fe and Ru (Roy & Saha, 1980); the complexes with Co and Hg (Poddar &

Ray, 1952); and those with Cu, Ag and Zn (Roy & Saha, 1980). The structures of HATU itself and of some simple salts derived from HATU have been reported recently (Janczak & Perpétuo, 2008a,b; Perpétuo & Janczak, 2008).

As a thiourea, HATU can be expected to undergo oxidation reactions yielding different products depending on the reaction conditions. Structure determinations undertaken so far concern the oxidation products only of substituted thioureas (e.g. Mamaeva & Bakibaev, 2003). In particular, Butler et al. (1978) determined the crystal structure of the so-called Hector's base (Hector, 1889) 5-imino-4-phenyl-3-phenyl-amino-4H-1,2,4-thiadiazoline, which was controversial for 100 years. Hector's bases are formed on oxidation of monoaryl-thioureas and on base-catalysed rearrangement yield 3,5-bis(arylamino)-1,2,4-thiadiazoles, known as Dost's bases (Christophersen et al., 1975; Butler et al., 1980, 1986).

Chilwana & Simoyi (2004) investigated the kinetics of 1-(diaminomethylene)thiourea oxidation with bromate(V) and iodate(VII) ions. In the case of the reaction with bromate(V) ions, 1-(diaminomethylene)urea was mentioned as the final product, whereas the reaction with iodate(VII) ions yields 3,5-diamino-1,2,4-thiadiazole, (I). The latter oxidation product is interestingly related to HATU as its cyclization product; however, no crystal structure determination has been attempted so far.
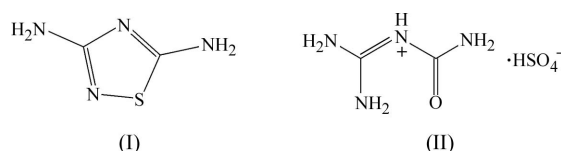
In this paper, the crystal structure of (I), obtained as a HATU oxidation product with a 3% aqueous solution of hydrogen peroxide, is reported. When 30% hydrogen peroxide was used, compound (II) could be isolated. Both (I) and (II) are of importance not only with respect to crystal engineering, but also in the design of new synthetic routes leading to HATU transition metal complexes. Compound (I) could be considered as the product of intramolecular N—S bond formation in the 1-(diaminomethylene)thiourea molecule (Fig. 1 and Table 1). This cyclization apparently does not lead to charge delocalization. As a result, the N1—C1 and N1—C2 bond lengths are not equal (Table 1). A literature survey leads to the conclusion that the most similar compound with available crystal structure data is 3,5-bis(diphenylamino)-
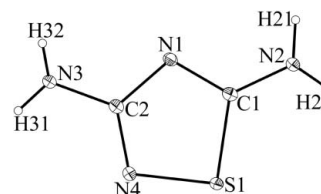

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

organic compounds

1,2,4-thiadiazole (Senda & Maruha, 1985), investigated during systematic studies on the oxidation of substituted thioureas by the iron(III) ion. This compound can be considered as the derivative of (I) with the H atoms of both amine groups replaced by phenyl rings. The 1,2,4-thiadiazole ring geometric parameters are in good agreement in the two compounds. In (I), all atoms constituting the 1,2,4-thiadiazole ring lie in one plane, whereas the two amine substituents (containing atoms N2 and N3) deviate from the ring plane by 0.036 (2) and 0.054 (2) Å (above and below the plane), respectively.

Molecules of (I) form hydrogen-bonded dimers linked through an N2—H21$\cdots$N1^{ii} (symmetry code as in Table 2) hydrogen bond to form $R_2^2(8)$ rings (Etter *et al.*, 1990), which are further linked through an N3—H31$\cdots$N4^i hydrogen bond with the formation of a second type of $R_2^2(8)$ ring (Fig. 2). The resulting molecular chains along [001] adopt a herring-bone-like arrangement in (I). Adjacent chains form very weak contacts between atom H32 at (x, y, z) and atom S1 at ($-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$).

Compound (II) is a salt consisting of 1-(diaminomethyl-ene)uronium cations and hydrogen sulfate anions. The cation, in comparison with the similar [HATUH]$^+$ cation present, for example, in 1-(diaminomethylene)thiouron-1-ium chloride (Perpétuo & Janczak, 2008), differs by the presence of an O atom (O1) instead of an S atom (Fig. 3). Atom O1 is involved
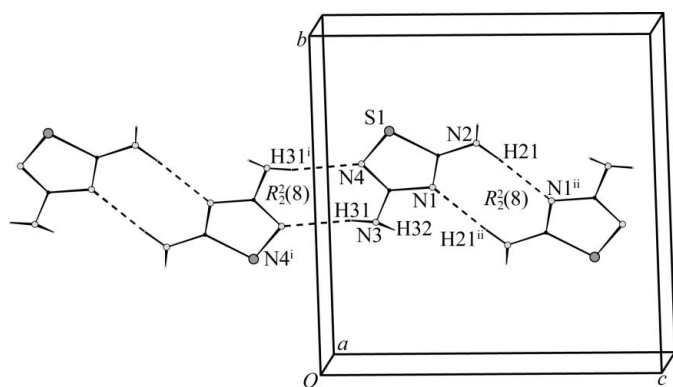
in an intramolecular N—H$\cdots$O hydrogen bond as an acceptor (Table 3). Thus, a hydrogen-bonded ring consisting of atoms N1, C1, C2, O1 and N4, lying in one plane, is formed. Atoms N2 and N3 from the amine groups bonded to atoms C1 and C2 deviate from this plane by 0.028 (2) and 0.035 (2) Å, respectively. The 1-(diaminomethylene)uronium cation geometrical parameters are consistent with the data reported for other salts [*e.g.* the sulfate hydrate (Lotsch & Schnick, 2005) and hydrogen chloride (Scoponi *et al.*, 1991)]. It is assumed that the cation is stabilized by π-electron delocalization, which is reflected by the C1—N1 and C2—N1 bond lengths [1.406 (2) and 1.366 (2) Å, respectively].

In the hydrogen sulfate anion, the H atom is statistically disordered over two half-occupied positions; in one position it is bonded to atom O31 and in the second position to atom O21. In both positions, this H atom participates in O—H$\cdots$O hydrogen bonds, with a hydrogen sulfate O atom involved as

(a)

Figure 2
Hydrogen bonds stabilizing molecular chains in (I). [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z$; (ii) $-x + 1$, $-y + 1$, $-z + 1$.]
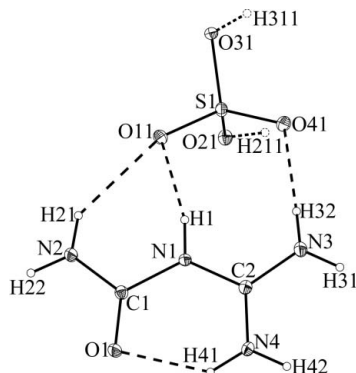

Figure 3
The cation and anion structure in (II). Hydrogen bonds and the disordered H atom are shown with dashed lines.
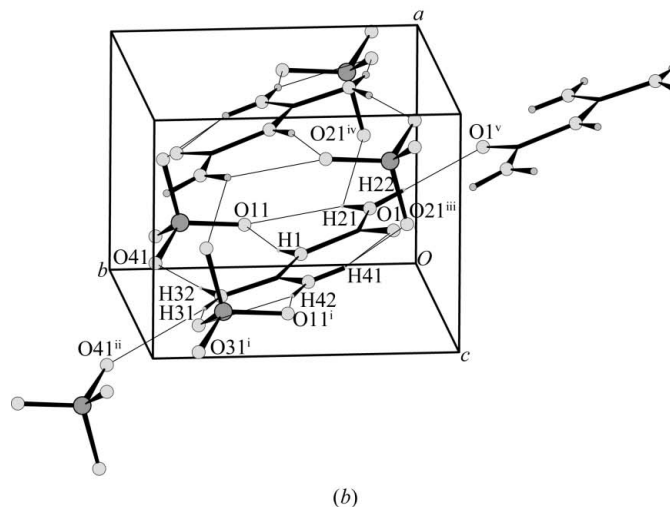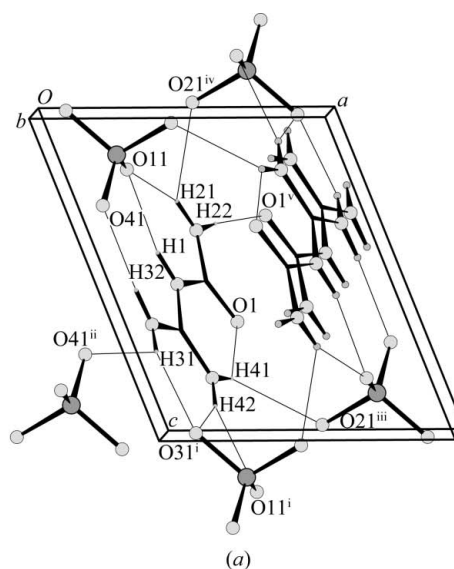

(b)

Figure 4
Two different views of the three-dimensional hydrogen-bonding network in (II). The disordered anion H atoms have been omitted for clarity. Hydrogen bonds are shown with thin lines. (Symmetry codes are as in Table 3.)

acceptor, to form anionic chains (Table 3). Similar hydrogen-bonded anionic chains were described for 1-(diaminomethylene)thiouron-1-ium hydrogen sulfate by Janczak & Perpétuo (2008b). Compound (II) is stabilized by an extensive network of N—H⋯O and O—H⋯O hydrogen bonds (Fig. 4). All amine H atoms from the organic cation are involved in these hydrogen bonds as donors. Characteristic motifs formed by the N2—H21⋯O11, N1—H1⋯O11 and N3—H32⋯O41 hydrogen bonds could be distinguished. Such motifs, within which $R_2^1(6)$ rings can be detected, are also present, for example, in 1-(diaminomethylene)thiouron-1-ium dihydrogen phosphate and dihydrogen arsenate (Janczak & Perpétuo, 2008b).

Experimental

HATU (0.5 g) was dissolved in a hydrogen peroxide aqueous solution (10 ml). An exothermal reaction occurred with evolution of a colourless gas. The product was obtained in the form of colourless crystals on slow evaporation of the reaction mixture. Compounds (I) and (II) formed when 3 or 30% hydrogen peroxide solutions were used, respectively. Analysis for (I) found: C 20.7, H 3.3, N 48.1, S 28.0%; $C_2H_4N_4S$ requires: C 20.7, H 3.4, N 48.3, S 27.6%; analysis for (II) found: C 13.1, H 4.3, N 30.9, S 14.4%; $C_2H_8N_4O_5S$ requires: C 12.0, H 4.0, N 28.0, S 16.0%.

Compound (I)

Crystal data

$C_2H_4N_4S$	$V = 450.7$ (7) Å^3
$M_r = 116.15$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 3.923$ (4) Å	$\mu = 0.56$ mm^{-1}
$b = 10.701$ (9) Å	$T = 100$ (2) K
$c = 10.754$ (9) Å	$0.21 \times 0.19 \times 0.18$ mm
$\beta = 93.40$ (8)°	

Data collection

Kuma KM-4 CCD diffractometer	960 reflections with $I > 2\sigma(I)$
3267 measured reflections	$R_{int} = 0.017$
1076 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	80 parameters
$wR(F^2) = 0.060$	All H-atom parameters refined
$S = 0.96$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
1076 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

S1—N4	1.6794 (15)	N2—C1	1.3389 (19)
S1—C1	1.7469 (18)	N3—C2	1.3674 (19)
N1—C1	1.3219 (19)	N4—C2	1.3199 (19)
N1—C2	1.377 (2)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H21⋯N1^{ii}	0.86 (2)	2.19 (2)	3.045 (3)	175 (2)
N3—H31⋯N4^{i}	0.82 (2)	2.18 (2)	2.965 (3)	161 (2)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$.

Compound (II)

Crystal data

$C_2H_7N_4O^+\cdot HSO_4^-$	$\gamma = 78.43$ (8)°
$M_r = 200.18$	$V = 358.0$ (5) Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.840$ (6) Å	Mo $K\alpha$ radiation
$b = 7.374$ (7) Å	$\mu = 0.45$ mm^{-1}
$c = 8.019$ (4) Å	$T = 100$ (2) K
$\alpha = 76.48$ (8)°	$0.35 \times 0.26 \times 0.24$ mm
$\beta = 66.48$ (6)°	

Data collection

Kuma KM-4 CCD diffractometer	2901 measured reflections
Absorption correction: analytical	1633 independent reflections
(*CrysAlis RED*; Oxford	1530 reflections with $I > 2\sigma(I)$
Diffraction, 2006)	$R_{int} = 0.017$
$T_{min} = 0.893, T_{max} = 0.904$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	111 parameters
$wR(F^2) = 0.077$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
1633 reflections	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O11	0.87	2.00	2.845 (2)	164
N2—H21⋯O11	0.87	2.30	3.056 (2)	145
N2—H21⋯O21^{iv}	0.87	2.48	2.963 (2)	116
N2—H22⋯O1^{v}	0.87	2.04	2.907 (3)	174
N3—H31⋯O31^{i}	0.87	2.21	3.022 (2)	155
N3—H31⋯O41^{ii}	0.87	2.53	3.052 (4)	119
N3—H32⋯O41	0.87	2.08	2.952 (3)	176
N4—H41⋯O1	0.87	1.99	2.656 (3)	133
N4—H41⋯O21^{iii}	0.87	2.40	3.067 (3)	134
N4—H42⋯O11^{i}	0.87	2.32	3.122 (2)	154
N4—H42⋯O31^{i}	0.87	2.43	3.172 (3)	144
O21—H211⋯O21^{vi}	0.84	1.73	2.558 (3)	168
O31—H311⋯O31^{vii}	0.84	1.72	2.550 (3)	171

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

All H atoms were easily found in a difference Fourier map. For (I), all H-atom positions and isotropic displacement parameters were refined [N—H = 0.81 (2)–0.86 (2) Å]. For (II), DFIX restraints were used for all N—H bond lengths (0.870 Å with an allowed deviation of 0.002 Å). Subsequently, the parameters for H atoms involved in N—H bonds were constrained using the AFIX 3 constraint. The hydrogen sulfate H atom was found to be disordered over two positions. Half-occupancy factors were assumed for both positions and AFIX 147 constraints were used for both disorder components. All H atoms were refined with U_{eq} values set at 1.2U_{eq}(parent atom). In the final difference maps, the following highest peaks were found: for (I) the maximum is 0.76 Å from atom C1, and for (II) the maximum is 0.69 Å from atom O21 and 0.86 Å from atom S1.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

organic compounds

References

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Version 3. Crystal Impact GbR, Bonn, Germany.

Butler, A. R., Edlund, U., Glidewell, C. & Nordén, B. (1986). *Acta Chem. Scand. Ser. B*, **40**, 779–781.

Butler, A. R., Glidewell, C., Hussain, I. & Maw, P. R. (1980). *J. Chem. Res. (S)*, pp. 114–115; *J. Chem. Res. (M)*, pp. 1843–1863.

Butler, A. R., Glidewell, C. & Liles, D. C. (1978). *Acta Cryst.* B**34**, 3241–3245.

Chakrabarty, K., Kar, T. & Sen Gupta, S. P. (1990). *Acta Cryst.* C**46**, 2065–2068.

Cheng, S.-T., Doxiadi, E., Vilar, R., White, A. J. P. & Williams, D. J. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2239–2244.

Chilwana, E. & Simoyi, R. H. (2004). *J. Chem. Phys. A*, **108**, 1024–1032.

Christophersen, C., Ottersen, T., Seff, K. & Treppendahl, S. (1975). *J. Am. Chem. Soc.* **97**, 5237–5241.

Diaz, P., Mingos, D. M. P., Vilar, R., White, A. J. P. & Williams, D. J. (2004). *Inorg. Chem.* **43**, 7597–7604.

Doxiadi, E., Vilar, R., White, A. J. P. & Williams, D. J. (2003). *Polyhedron*, **22**, 2991–2998.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Gale, P. A. & Quesada, R. (2006). *Coord. Chem. Rev.* **250**, 3219–3244.

Gimeno, N. & Vilar, R. (2006). *Coord. Chem. Rev.* **250**, 3161–3189.

Hector, D. S. (1889). *Chem. Ber.* **22**, 1176–1180.

Janczak, J. & Perpétuo, G. J. (2008*a*). *Acta Cryst.* C**64**, o114–o116.

Janczak, J. & Perpétuo, G. J. (2008*b*). *Acta Cryst.* C**64**, o330–o334.

Kabir, M. K., Yamada, K., Adachi, K., Kondo, M. & Kawata, S. (2002). *Acta Cryst.* E**58**, m580–m582.

Lankshear, M. D. & Beer, P. D. (2006). *Coord. Chem. Rev.* **250**, 3142–3160.

Lotsch, B. V. & Schnick, W. (2005). *Z. Anorg. Allg. Chem.* **631**, 2967–2969.

Mamaeva, E. A. & Bakibaev, A. A. (2003). *Tetrahedron*, **59**, 7521–7525.

Oxford Diffraction (2006). *CrysAlis RED* and *CrysAlis CCD*. Oxford Diffraction Poland, Wrocław, Poland.

Perpétuo, G. J. & Janczak, J. (2008). *Acta Cryst.* C**64**, o264–o268.

Poddar, S. N. & Ray, R. (1952). *J. Indian Chem. Soc.* **29**, 279–290.

Roy, N. K. & Saha, Ch. R. (1980). *J. Inorg. Nucl. Chem.* **42**, 37–42.

Scoponi, M., Polo, E., Bertolasi, V., Carassiti, V. & Bertelli, G. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 1619–1624.

Senda, H. & Maruha, J. (1985). *Acta Cryst.* C**41**, 1329–1331.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Trochimczuk, A. W. & Kolarz, B. N. (2000). *Eur. Polym. J.* **36**, 2359–2363.

Vilar, R., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (1998). *Angew. Chem. Int. Ed.* **37**, 1258–1261.

Vilar, R., Mingos, D. M. P., White, A. J. P. & Williams, D. J. (1999). *Chem. Commun.* pp. 229–230.