Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}
O1	0.45345 (11)	0.34734 (11)	0.46771 (4)	0.0295 (2)
O3	0.71802 (11)	0.37425 (12)	0.45992 (4)	0.0360 (3)
N13	0.58101 (13)	0.42137 (13)	0.44737 (5)	0.0259 (3)
O2	0.57188 (12)	0.54138 (11)	0.41409 (4)	0.0318 (3)
N5	0.23471 (14)	0.58389 (13)	0.39398 (5)	0.0241 (3)
N4	−0.03208 (14)	0.55287 (14)	0.39738 (5)	0.0272 (3)
N6	0.11014 (17)	0.38727 (15)	0.45794 (5)	0.0318 (3)
C14	0.10383 (16)	0.50091 (16)	0.41909 (6)	0.0248 (3)
C13	0.18101 (16)	0.69372 (15)	0.35482 (6)	0.0240 (3)
C8	0.01059 (17)	0.67478 (16)	0.35729 (6)	0.0263 (3)
C10	0.0014 (2)	0.88218 (19)	0.28813 (7)	0.0374 (4)
C12	0.26427 (18)	0.80605 (17)	0.31859 (6)	0.0294 (3)
C9	−0.08244 (19)	0.76859 (18)	0.32407 (6)	0.0327 (4)
C11	0.1712 (2)	0.90002 (18)	0.28540 (7)	0.0362 (4)
O6	−0.06934 (11)	0.15155 (11)	0.53324 (4)	0.0305 (3)
O4	0.18970 (12)	0.12266 (12)	0.54138 (5)	0.0363 (3)
O5	0.01333 (12)	−0.04191 (11)	0.58753 (4)	0.0320 (3)
N14	0.04474 (13)	0.07695 (13)	0.55388 (5)	0.0252 (3)
N2	−0.59968 (14)	−0.05858 (14)	0.60191 (5)	0.0267 (3)
N1	−0.33583 (15)	−0.08941 (13)	0.60816 (5)	0.0252 (3)
N3	−0.41634 (17)	0.10871 (15)	0.54349 (5)	0.0325 (3)
C1	−0.41704 (17)	−0.20021 (16)	0.64635 (6)	0.0252 (3)
C7	−0.44900 (16)	−0.00627 (15)	0.58188 (6)	0.0246 (3)
C2	−0.35952 (19)	−0.31213 (17)	0.68367 (6)	0.0306 (3)
C6	−0.58499 (17)	−0.18177 (16)	0.64188 (6)	0.0259 (3)
C5	−0.70145 (19)	−0.27753 (18)	0.67314 (6)	0.0321 (3)
C3	−0.4761 (2)	−0.40767 (19)	0.71519 (7)	0.0354 (4)
C4	−0.6438 (2)	−0.39182 (19)	0.70992 (7)	0.0364 (4)
O8	0.64601 (12)	0.04581 (10)	0.03338 (4)	0.0291 (2)
O7	0.45100 (12)	−0.06507 (11)	0.08886 (4)	0.0313 (2)
O9	0.61867 (13)	−0.21529 (11)	0.04423 (4)	0.0344 (3)
N15	0.57109 (14)	−0.07823 (13)	0.05551 (5)	0.0245 (3)
N7	0.40688 (13)	0.26941 (14)	0.10796 (5)	0.0237 (3)
N8	0.44777 (14)	0.53218 (14)	0.10331 (5)	0.0258 (3)
C21	0.49525 (16)	0.39521 (15)	0.08222 (6)	0.0243 (3)
N9	0.60952 (15)	0.38405 (17)	0.04314 (5)	0.0311 (3)
C20	0.32215 (17)	0.49617 (16)	0.14336 (6)	0.0261 (3)
C16	0.17815 (17)	0.25133 (19)	0.18216 (6)	0.0300 (3)
C15	0.29662 (16)	0.32755 (15)	0.14620 (6)	0.0238 (3)
C19	0.22998 (19)	0.59233 (19)	0.17586 (6)	0.0329 (4)
C17	0.08478 (19)	0.3477 (2)	0.21454 (7)	0.0365 (4)
C18	0.1105 (2)	0.5153 (2)	0.21165 (7)	0.0385 (4)
O12	0.84627 (12)	−0.43551 (11)	−0.03187 (4)	0.0296 (2)
O11	0.87556 (12)	−0.69045 (11)	−0.04162 (4)	0.0342 (3)
O10	1.04316 (12)	−0.51490 (11)	−0.08668 (4)	0.0308 (2)
N10	1.04760 (14)	0.09131 (14)	−0.10002 (5)	0.0254 (3)
N11	1.08726 (13)	−0.16853 (14)	−0.10569 (5)	0.0232 (3)
N16	0.92259 (14)	−0.54671 (13)	−0.05341 (5)	0.0243 (3)
N12	0.88922 (15)	−0.09343 (17)	−0.03927 (5)	0.0291 (3)
C28	1.00137 (16)	−0.05875 (15)	−0.07909 (6)	0.0228 (3)
C22	1.16864 (16)	0.07937 (16)	−0.14123 (6)	0.0253 (3)
C26	1.30451 (17)	−0.14076 (18)	−0.18379 (6)	0.0293 (3)
C27	1.19325 (16)	−0.08653 (16)	−0.14554 (6)	0.0236 (3)
C23	1.25799 (19)	0.19591 (18)	−0.17447 (6)	0.0320 (3)
C24	1.3708 (2)	0.1414 (2)	−0.21231 (7)	0.0360 (4)
C25	1.39270 (19)	−0.0240 (2)	−0.21716 (7)	0.0349 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O5	0.88 (2)	1.99 (2)	2.871 (2)	176 (2)
N2—H02···O4^{i}	0.91 (2)	1.94 (2)	2.778 (2)	154 (2)
N3—H03*A*···O6	0.95 (2)	1.92 (2)	2.842 (2)	162 (2)
N3—H03*B*···O1^{i}	0.88 (2)	2.17 (2)	2.915 (2)	142 (1)
N4—H04···O3^{i}	0.84 (2)	2.02 (2)	2.800 (2)	153 (2)
N5—H05···O2	0.90 (2)	1.97 (2)	2.870 (2)	178 (2)
N6—H06*A*···O1	0.93 (2)	1.96 (2)	2.859 (2)	160 (2)
N6—H06*B*···O6	0.85 (2)	2.17 (2)	2.902 (2)	144 (2)
N7—H07···O7	0.90 (2)	1.97 (2)	2.874 (2)	176 (2)
N8—H08···O9^{ii}	0.91 (2)	1.89 (2)	2.757 (2)	159 (2)
N9—H09*A*···O8	0.92 (2)	1.97 (2)	2.848 (2)	160 (2)
N9—H09*B*···O12^{ii}	0.85 (2)	2.16 (2)	2.899 (2)	146 (2)
N10—H010···O11^{ii}	0.91 (2)	1.87 (2)	2.754 (2)	162 (2)
N11—H011···O10	0.93 (2)	1.95 (2)	2.879 (2)	177 (2)
N12—H12*A*···O8	0.86 (2)	2.16 (2)	2.904 (2)	144 (2)
N12—H12*B*···O12	0.91 (2)	1.96 (2)	2.839 (2)	164 (2)

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

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS* in *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1323). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1328–1330

N-(2-Pyridinium)urea nitrate†

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Abstract

The *N*-(2-pyridinium)urea cation of the title compound, $C_6H_8N_3O^+\cdot NO_3^-$, is planar within 0.044 (2) Å and adopts an *s-cis–s-cis* conformation with respect to the imino C—N bonds. The hydrogen-bonding network results in layers parallel to the (203) plane.

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† Alternative name: 2-ureidopyridinium nitrate.

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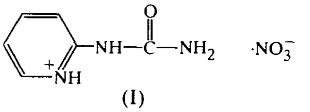
Comment

This article is part of a project investigating adducts of unsymmetrically substituted (by π-conjugated substituents) urea derivatives and inorganic salts with potential as non-linear materials. The adducts of *N*-(2-pyridyl)urea (2pU) with $HReO_4$ and $HClO_4$ were found to crystallize in the centrosymmetric space groups $P\bar{1}$ and $P2_1/n$, respectively (Velikova, Petrova & Angelova, 1997), and contain cationic hydrogen-bonded dimers. In these structures, three O atoms from the tetrahedron are involved in hydrogen bonds. Here, in the title structure, (I), we exchanged the counter-ion with a planar NO_3^- anion in order to investigate its effect on the cationic arrangement.



(I)

Bond lengths and angles in *N*-(2-pyridinium)urea nitrate are similar to those found for *N*-(2-pyridyl)urea (2pU) (Velikova, Angelova & Kossev, 1997) and derivatives (Le Magueres *et al.*, 1994; Velikova, Petrova & Angelova, 1997; Velikova, Angelova, Petrova & Kossev, 1997). The cation is planar, with the largest deviation of 0.044 (2) Å at the O1 atom. The overall conformation of the molecule can be described as *s-cis–s-cis* with respect to the imino C1—N2—C2 bonds due to protonation of the *endo*-N atom and formation of an intramolecular hydrogen bond. The same conformation is found in the structures of *N*-(2-pyridinium)urea perrhenate and perchlorate.

The ions are organized in layers parallel to (203) by an extensive hydrogen-bonding network (Table 2). The structural units are held together by two types of hydrogen bonds. The first is between the *cisoid* imino HN2 and amino HN31 atoms, and two O atoms from the anion, forming an eight-membered hydrogen-bonded ring similar to those found in the structures of $2pUH^+ \cdot ClO_4$ and thiourea inclusion compounds (Li & Mak, 1996). The second type of hydrogen bond is maintained by a symmetrically bifurcated HN32 with two nitrate O atoms, forming a four-membered hydrogen-bonded ring with an $O2\cdots HN32^{iii}\cdots O3$ angle of 52.7 (5)° [symmetry code: (iii) $-\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$]. These hydrogen bonds form ribbons extended along the *b* axis. In addition, $2pUH^+$ cations are linked to other $2pUH^+$ cations from adjacent ribbons through a centrosymmetric four-membered hydrogen-bonded ring including H atoms of the protonated *endo*-N atoms. These rings are similar to those found in the structure of 3-aminopyrazine-2-carboxylic acid (Dobson & Gerkin, 1996). Such an interaction between the cations is quite different from those in the structures of other salts of 2-pyridylurea where the cations are held together by a centrosymmetric eight-membered cycle including amino N atoms. The cohesion of the layers is realized by stacking of the carbonyl groups which are separated by 3.10 (2) Å.

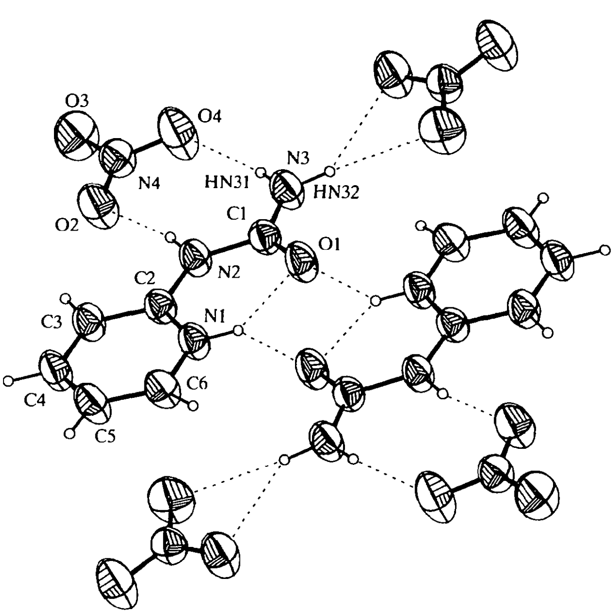


Fig. 1. View of the title structure and the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

An equimolar mixture of *N*-(2-pyridyl)urea (1 g) and HNO_3 (0.51 ml) was stirred at 303 K for 30 min. A single crystal was grown by slow evaporation at room temperature.

Crystal data

$C_6H_8N_3O^+ \cdot NO_3^-$
$M_r = 200.16$
Monoclinic
$P2_1/n$
$a = 5.0861\ (10)$ Å
$b = 12.198\ (2)$ Å
$c = 13.760\ (2)$ Å
$\beta = 96.070\ (15)°$
$V = 848.8\ (3)$ Å^3
$Z = 4$
$D_x = 1.566$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 20.55–21.45°$
$\mu = 0.133$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.45 × 0.40 × 0.27 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3950 measured reflections
1862 independent reflections
1348 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 27.95°$
$h = 0 \rightarrow 6$
$k = -16 \rightarrow 16$
$l = -11 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.134$
$S = 1.068$
1862 reflections
151 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 0.0869P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.230$ e Å^{-3}
$\Delta\rho_{\min} = -0.251$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.2300 (19)	N4—O3	1.2265 (19)
N2—C2	1.359 (2)	N4—O4	1.237 (2)
N2—C1	1.394 (2)	N4—O2	1.2400 (19)
N3—C1	1.324 (2)		
C2—N2—C1	125.93 (14)	N1—C2—N2	120.39 (14)
O1—C1—N3	124.50 (16)	N1—C2—C3	118.35 (15)
O1—C1—N2	121.18 (15)	N2—C2—C3	121.26 (15)
N3—C1—N2	114.32 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—HN1···O1	0.85 (2)	1.95 (2)	2.6221 (19)	135.1 (18)
N1—HN1···O1^{i}	0.85 (2)	2.34 (2)	2.9417 (18)	127.9 (17)
N2—HN2···O2	0.86 (2)	1.97 (2)	2.820 (2)	168 (2)
N3—HN31···O4	0.88 (2)	2.10 (2)	2.971 (2)	168.0 (17)
N3—HN32···O3^{ii}	0.89 (2)	2.33 (2)	3.210 (2)	171.7 (17)
N3—HN32···O2^{ii}	0.89 (2)	2.47 (2)	3.155 (2)	134.8 (16)

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

H atoms were localized from difference Fourier maps and refined with fixed $U_{\rm iso} = 0.0506$ Å^2.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *DATARED* (Vassilev, unpublished). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1296). Services for accessing these data are described at the back of the journal.

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A dithiadiazolylium chloride salt from the reaction of 4-phenyl-1,2,3,5-dithiadiazolyl with gold(I) chloride

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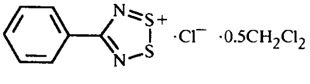
Abstract

4-Phenyl-1,2,3,5-dithiadiazolyl reacts with AuCl·THT (THT is tetrahydrothiophene) to produce 4-phenyl-1,2,3,5-dithiadiazolylium chloride and elemental gold. The structure of the dichloromethane hemisolvate, $C_7H_5N_2S_2^+\cdot Cl^-\cdot 0.5CH_2Cl_2$ or $PhCNSSN^+\cdot Cl^-\cdot 0.5CH_2Cl_2$, contains one Cl^- anion per dithiadiazolylium cation. The Cl^- anion sits approximately equidistant from each of the S atoms of the CN_2S_2 fragment, and lies almost directly in the heterocyclic ring plane. The solvent molecule is well ordered, forming weak interactions with the dithiadiazolium and Cl^- ions.

Comment

Recently, we have been investigating the oxidative addition reactions of 4-phenyl-1,2,3,5-dithiadiazolyl radicals to late transition metal elements (Banister *et al.*, 1998), in which the dithiadiazolyl is bound directly to the metal following sulfur–sulfur bond cleavage of the ligand. The reaction of 4-phenyl-1,2,3,5-dithiadiazolyl with AuCl·THT (THT is tetrahydrothiophene) in dichloromethane produced a yellow crystalline solid, which was identified by a single-crystal X-ray diffraction study as $PhCNSSN^+\cdot Cl^-\cdot 0.5CH_2Cl_2$, (1).



(1)

The average S—S, S—N and C—N distances [2.0115 (13), 1.593 (3) and 1.345 (4) Å, respectively] are

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