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Structure of an Oxonium Salt Crystal Complex

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Abstract

The title complex is composed of two compounds, oxonium 1-cyano-2-hydrazino-2-oxoethane-1-nitronate and 3-amino-4-nitro-1,2-dihydro-5-pyrazolone monohydrate (1). The anion is nearly planar and is stabilized by delocalization of the negative charge. The oxonium ion is involved in an O—H···N hydrogen bond to the terminal N atom in the hydrazide group. The pyrazolone rings and the anions stack nearly parallel to the 101 plane in the crystal structure which is stabilized by intermolecular hydrogen bonds.

Comment

2-Cyano-2-nitroacetohydrazide monohydrate (2) was first synthesized and described by Darapsky & Hillers (1915); there are five plausible tautomeric forms. The present investigation is part of a study of aliphatic nitro compounds with acid properties and has been undertaken in order to determine the actual tautomeric form of (2). The investigation revealed that the title complex (1) is a crystal composed of two compounds, (2) and the isomeric 3-amino-4-nitro-1,2-dihydro-5-pyrazolone (3). This is comprehensible as (2) easily rearranges to (3) by heating or by standing in solution at room temperature (Darupsky & Hillers, 1915).

Bond distances and bond angles for the anion are given in Table 2. The structural formula with the atomic numbering scheme is shown in Fig. 1. The sum of the angles around C2 is 360 (1)° and a least-squares plane defined by all non-H atoms in (2) apart from N4 reveals a nearly planar system with a maximum distance of -0.06 Å (for O3) from the least-squares plane. Hence C2 is sp^2-hybridized. In Table 3, a comparison is made between selected bond distances in (1) and the corresponding bonds in related compounds. The table shows the effect on cyanoacetohydrazide bond lengths of substituting H with a nitro group at C2: C1—C2 and C2—C3 are shortened, C3—N3 is elongated, C1—O1 is unchanged and C1—N1 is probably extended by 0.02 Å. The C2—N2 length [1.357 (8) Å] is characteristic of a C—N partial double bond and is comparable to the corresponding bond [1.327 (4) Å] in the nitromalonamide anion (Simonsen, 1981). Three resonance formulae are proposed to describe the delocalization of the negative charge in (2), each with

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.4313 (8)	0.4197 (6)	0.4031 (3)	0.036 (4)
O2	0.6718 (8)	0.7273 (6)	0.1461 (4)	0.043 (5)
O3	0.7342 (9)	0.4724 (6)	0.0753 (3)	0.045 (5)
O4†	0.0683 (9)	0.6443 (7)	0.5591 (4)	0.048 (5)
O15	0.9282 (8)	0.9296 (6)	−0.3253 (3)	0.038 (4)
O41‡	0.7478 (9)	0.9089 (7)	0.4645 (4)	0.043 (5)
O141	0.9440 (9)	1.3127 (7)	−0.2909 (4)	0.055 (5)
O142	0.8259 (9)	1.3751 (7)	−0.1409 (4)	0.051 (5)
N1	0.502 (1)	0.7107 (7)	0.3326 (4)	0.033 (5)
N2	0.673 (1)	0.5501 (8)	0.1529 (4)	0.030 (5)
N3	0.606 (1)	0.0896 (8)	0.2398 (4)	0.041 (6)
N4	0.3988 (9)	0.7958 (7)	0.4165 (4)	0.030 (5)
N11	0.861 (1)	0.7620 (7)	−0.1679 (4)	0.033 (5)
N12	0.800 (1)	0.8042 (8)	−0.0718 (4)	0.031 (5)
N13	0.743 (1)	1.081 (1)	0.0062 (4)	0.043 (6)
N14	0.8736 (9)	1.2625 (8)	−0.2005 (5)	0.035 (5)
C1	0.505 (1)	0.5236 (9)	0.3305 (5)	0.023 (5)
C2	0.597 (1)	0.4493 (9)	0.2399 (5)	0.025 (6)
C3	0.603 (1)	0.251 (1)	0.2393 (5)	0.030 (6)
C13	0.796 (1)	0.9907 (9)	−0.0722 (5)	0.029 (6)
C14	0.856 (1)	1.0708 (9)	−0.1717 (5)	0.024 (5)
C15	0.890 (1)	0.9257 (9)	−0.2328 (5)	0.030 (6)

†H_2O.
‡H_3O^+.

Table 2. *Geometric parameters* (Å, °)

(2)			
O1—C1	1.220 (7)	N2—C2	1.357 (8)
O2—N2	1.260 (7)	N3—C3	1.157 (9)
O3—N2	1.272 (7)	C1—C2	1.446 (9)
N1—N4	1.419 (8)	C2—C3	1.42 (1)
N1—C1	1.346 (8)		
N4—N1—C1	121.1 (5)	N1—C1—C2	118.2 (5)
O2—N2—O3	118.3 (5)	N2—C2—C1	126.9 (6)
O2—N2—C2	119.9 (5)	N2—C2—C3	115.4 (6)
O3—N2—C2	121.7 (6)	C1—C2—C3	117.7 (5)
O1—C1—N1	120.8 (6)	N3—C3—C2	179.2 (7)
O1—C1—C2	121.0 (6)		
(3)			
O15—C15	1.268 (9)	N12—C13	1.334 (9)
O141—N14	1.273 (8)	N13—C13	1.33 (1)
O142—N14	1.223 (8)	N14—C14	1.385 (8)
N11—N12	1.399 (8)	C13—C14	1.422 (9)
N11—C15	1.376 (8)	C14—C15	1.42 (1)
N12—N11—C15	110.4 (5)	N13—C13—C14	127.6 (6)
N11—N12—C13	109.3 (5)	N14—C14—C13	123.1 (6)
O141—N14—O142	122.7 (6)	N14—C14—C15	127.4 (6)
O141—N14—C14	116.5 (6)	C13—C14—C15	109.5 (6)
O142—N14—C14	120.9 (6)	O15—C15—N11	123.3 (7)
N12—C13—N13	125.7 (6)	O15—C15—C14	132.6 (6)
N12—C13—C14	106.7 (6)	N11—C15—C14	104.0 (6)

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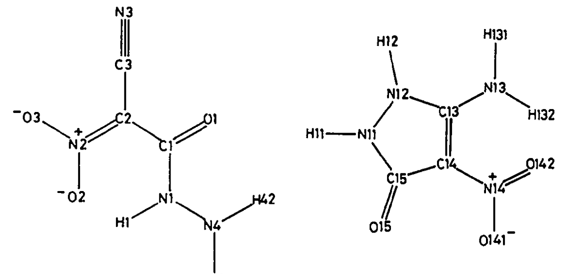
Table 3. *Selected bond lengths* (Å) *in* (1) *compared with corresponding bonds in related compounds*

Compound	Ref.	N1—C1	C1—C2	C2—C3	C3—N3
(1)		1.346 (8)	1.446 (9)	1.42 (1)	1.157 (9)
$NCCH_2CONHNH_2$	*a*	1.330 (5)	1.524 (5)	1.453 (5)	1.122 (5)
$NCCH_2CONH_2$	*b*	1.326 (7)	1.524 (7)	1.440 (7)	1.142 (7)
		1.327 (7)	1.519 (7)	1.461 (7)	1.134 (7)
$H_2NCONHNH_2$	*c*	1.346 (2)			
$H_2NCONHNH_3^+$	*c*	1.379 (2)			
$H_2NCONHNH_3^+$	*d*	1.382 (4)			

References: (*a*) Chieh (1973). (*b*) Chieh & Trotter (1970). (*c*) Gubin *et al.* (1986). (*d*) Roul, Choudhary, Rajagopal & Sequeira (1987).



(2) (3)

Fig. 1. Structural formula and atomic numbering scheme for (3) and the anion of (2).

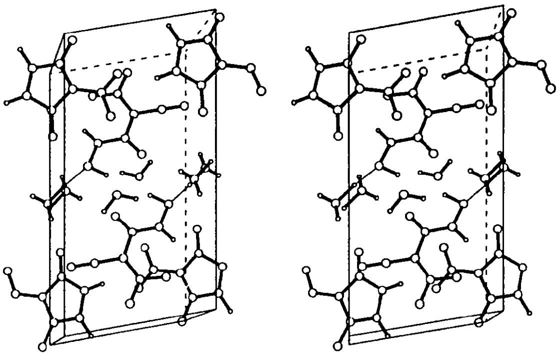


Fig. 2. Stereo drawing (*ATOMS*2.0, Dowty, 1991) of one unit cell of (1). Only the O41—H···N4 hydrogen bond is shown.

a double bond extending from C2 (Fig. 1 gives the C2=N2 resonance form; formulae with C2=C3 and C2=C1 double bonds are not shown).

A weak difference electron-density peak was located at the H413 position but as a result of problems with the refinement of the H atoms, there is some doubt as to whether the 'acidic' H413 atom belongs to O41 or N4, forming an oxonium salt or an inner salt respectively. Table 3 gives some distances in semicarbazide and semicarbazide hydrochloride; C1—N1 is approximately 0.034 Å longer in the hydrochloride than in semicarbazide while it is exactly the same length in (2) as in the semicarbazide suggesting the oxonium salt structure. The bond distances and bond angles in the pyrazolone molecule (3) are approximately the same as those found by Mogensen & Simonsen (1991).

Experimental

Crystal data

$H_3O^+.C_3H_3N_4O_4^-.$-
$C_3H_4N_4O_3.H_2O$
M_r = 324.22
Triclinic
$P\bar{1}$
a = 6.511 (4) Å
b = 7.180 (5) Å
c = 14.01 (1) Å
α = 80.57 (7)°
β = 78.93 (6)°
γ = 81.55 (5)°
V = 629 (1) Å^3
Z = 2
D_x = 1.710 Mg m^{-3}

D_m = 1.69 (2) Mg m^{-3}
Density measured by flotation in a mixture of CCl_4 and CH_2BrCl
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 3.74–17.55°
μ = 0.147 mm^{-1}
T = 295 K
Needle (cut)
0.33 × 0.23 × 0.07 mm
Colourless

Data collection

Enraf-Nonius CAD-4F diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2445 measured reflections
2445 independent reflections
1195 observed reflections [$I>2.5\sigma(I)$]
$\theta_{\max}$ = 26°

$h = 0 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 17$
1 (intensity) standard reflection
frequency: 180 min
intensity decrease: 4.3%
3 (orientation) standard reflections
monitored every 100 reflections
intensity variation: 6.1%

Refinement

Refinement on F
Final R = 0.082
wR = 0.0696
S = 3.0
2086 reflections
214 parameters
Only coordinates of H atoms refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max}$ = 0.18
$\Delta\rho_{\max}$ = 0.6 e Å^{-3}
$\Delta\rho_{\min}$ = −0.5 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data reduction: *Xtal*3.0 *ADDREF*, *SORTRF* (Hall & Stewart, 1990) and Norrestam & Nielson (1982). Program(s) used to solve structure: *Xtal*3.0. Program(s) used to refine structure: *Xtal*3.0 *CRYLSQ*. Software used to prepare material for publication: *Xtal*3.0 *BONDLA*, *CIFIO* and *ATABLE*.

Positional H-atom parameters for ten of the twelve H atoms were determined from $\Delta\rho$ maps, the two missing H atoms being H41 and H132. Five of the localized H atoms refined to 'unrealistic' bond lengths and so were fixed at their initial positions.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55236 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1010]

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Structure of a Polydentate Alkoxide Ligand, *cis*-Tetrahydroxytetramethylcyclobutane

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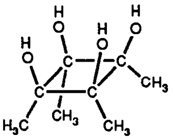
Abstract

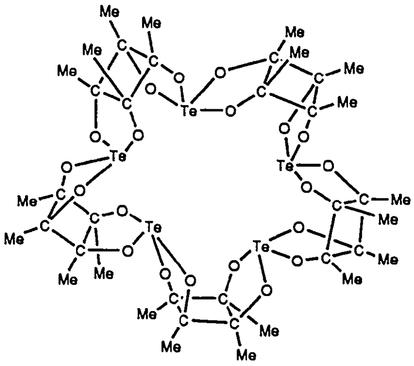
Molecules of the title compound, 1β,2β,3β,4β-tetramethylcyclobutane-1α,2α,3α,4α-tetraol, assume a layered structure with intermolecular hydrogen bonding and $CH_3\cdots CH_3$ van der Waals contacts. Some intramolecular hydrogen bonding is also observed. The cyclobutane ring is folded to the extent of 18–19° along the diagonal of the ring.

Comment

In our search for polydentate alkoxide ligands, we have identified the tetraol $Me_4C_4(OH)_4$ (1) as a candidate for the formation of a square-pyramidal complex such as $Me_4C_4O_4W{=}O$. The properties of such a complex would be of interest because there are no known complexes of a tetradentate alkoxide ligand. A complex of this unique ligand may possess unusual reactivity or be a model of metal oxide catalysis. The only known complex of (1) is a pentameric tellurane (2) in which each tetraol complexes two Te atoms in a bidentate fashion rather than in the tetradentate mode (Kahle, 1987). Reasons for this may be the preference of Te^{IV} for a 'seesaw' coordination geometry, which tetradentate (1) cannot assume, or the tendency of cyclobutanes to ring pucker [both in the solid state (Allen, 1984) and in the gas phase (Legon, 1980)]. If (1) binds as a tetradentate ligand, the degree of ring puckering may be less than in the bidentate mode.

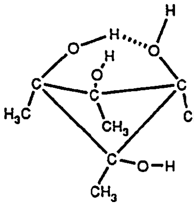


(1)



(2)

We undertook the X-ray crystal structure determination of (1) to gain insight into why the tetraol binds as in (2) and also to obtain an indication of the strength of the ring-puckering tendency in the uncomplexed ligand. In addition, the nature of the hydrogen bonding and its influence on the degree of ring puckering of uncomplexed (1) was of interest. Intramolecular hydrogen bonding between two diagonally positioned hydroxy groups of (1) might influence the degree of ring puckering because the puckering brings the hydroxy groups closer together as shown in (3).



(3)

The structure consists of bilayers of tetraol molecules having inter- and intramolecular hydrogen bonds and $CH_3\cdots CH_3$ van der Waals contacts (Fig. 2). There are two half molecules of tetraol in the asymmetric unit. One of the whole molecules is shown in Fig. 1. In each molecule, a crystallographic mirror plane passes through two O atoms and two C atoms of the four-membered ring and their two bonded methyl groups. The H atoms of the latter

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