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Monoclinic and triclinic concomitant polymorphs of di-μ-pyridazine-$1\kappa^2N$:$2\kappa^2N'$-bis[(saccharinato)silver(I)]

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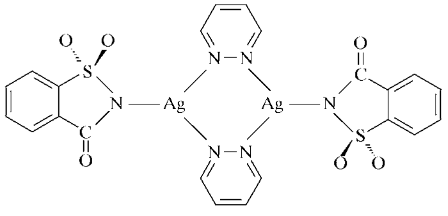
Crystallization of the title compound, di-μ-pyridazine-$1\kappa^2N$:-$2\kappa^2N'$-bis[(2,3-dihydro-3-oxobenzisosulfonazolato-κN)silver(I)], $[Ag_2(C_7H_4NO_3S)_2(C_4H_4N_2)_2]$, from acetonitrile yields both monoclinic, (I), and triclinic, (II), polymorphs. In both forms, the silver(I) ions have a slightly distorted trigonal AgN_3 coordination geometry and are doubly bridged by two neutral pyridazine (pydz) ligands, generating a centrosymmetric dimeric structure. The saccharinate (sac) ligands are *N*-coordinated. The dihedral angles between the sac and pydz rings are 8.43 (7) and 7.94 (8)° in (I) and (II), respectively, suggesting that the dimeric molecule is nearly flat. The bond geometry is similar in both polymorphs. In (I), the dimers interact with each other *via* aromatic π_{sac}–π_{pydz} stacking interactions, forming two-dimensional layers, which are further crosslinked by weak C—H$\cdots$O interactions. Compound (II) exhibits similar C—H$\cdots$O and π–π interactions, but additional C—H$\cdots\pi$ and $\pi\cdots$Ag interactions help to stabilize the packing of the dimers.

Comment

Saccharin, alternatively named 1,2-benzisothiazolin-3(2*H*)-one 1,1-dioxide, is one of the best known and most widely used non-caloric sweeteners and food additives. Owing to its potential harmfulness and especially its suspected carcinogenic nature (Cohen-Addad *et al.*, 1986; Suzuki & Suzuki, 1995), saccharin is probably one of the most studied components of the food supply. It has been shown that the deprotonated form of saccharin, saccharinate (sac), acts as a polyfunctional ligand through four sites, *viz.* the negatively charged imine N atom, and one carbonyl and two sulfonyl O atoms. The sac ligand can behave as a mono-, bi- or tridentate ligand, and in some cases also as a bridging ligand between metal ions (Baran, 2005; Baran & Yilmaz, 2005). As part of our study on the synthesis and the spectral, thermal and crystallographic characterization of metal complexes of sac, an attempt to synthesize a silver(I) complex of sac with pyridazine (pydz) resulted in the concurrent crystallization, from acetonitrile, of monoclinic, (I), and triclinic, (II), forms of the title compound as concomitant polymorphs.



(I)/(II)

Visual examination of the crystals under a microscope indicated that most of the crystals (*ca* 90%) consisted of (I). Data collections performed at 293 K produced the same outcome, indicating that the polymorphism observed in the title compound is not associated with a temperature phase transition. In both (I) and (II), the silver(I) ions have a slightly distorted trigonal AgN_3 coordination geometry and are doubly bridged by two neutral pyridazine (pydz) ligands, forming a centrosymmetric dimeric structure. The anionic sac ligands are *N*-coordinated. The sac (atoms C1–C7, N1 and S1) and pydz (atoms C8–C11, N2 and N3) ligands are both essentially planar, and the dihedral angles between the mean planes of these ligands are 8.43 (7) and 7.94 (8)° in (I) and (II), respectively, suggesting that the dimeric molecule is nearly flat. The bond geometry is similar in the two polymorphs. The average intradimer Ag$\cdots$Ag distance of 3.706 (2) Å in (I) and (II) is much longer than the upper limit of 3.30 Å reported by Jansen (1987) for an Ag$\cdots$Ag contact in silver(I) complexes. The Ag—N_{sac} bond distances in (I) and (II) are similar to those found in $[Ag_2(sac)_2(hep)_2]_n$ [2.1718 (17) and 2.1819 (17) Å; hep is *N*-(2-hydroxyethyl)piperazine; Hamamci *et al.*, 2005*a*], $[Ag_2(sac)_2(pyet)_2]$ [2.1444 (12) Å; pyet is 2-pyridylethanol; Yilmaz *et al.*, 2005] and $[Ag(sac)(py)]_n$ [2.084 (2) Å; py is pyridine; Hamamci *et al.*, 2005*b*], but significantly shorter than those reported for $[Ag_2(sac)_2(aepy)_2]$ [2.449 (2) Å; aepy is 2-(2-aminoethyl)pyridine; Hamamci *et al.*, 2005*c*].

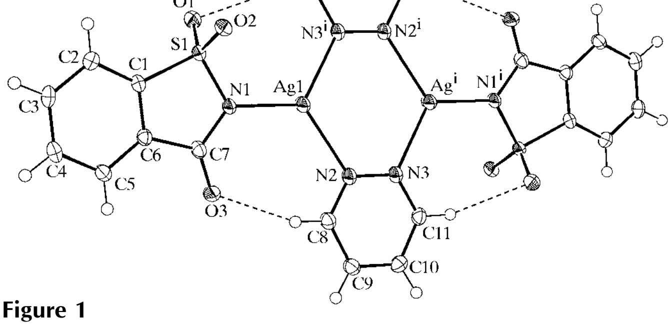


Figure 1
The molecule of (I), showing the atom-labelling scheme (50% probability displacement ellipsoids). Hydrogen bonds are shown as dashed lines. (The symmetry code is as in Table 1.)

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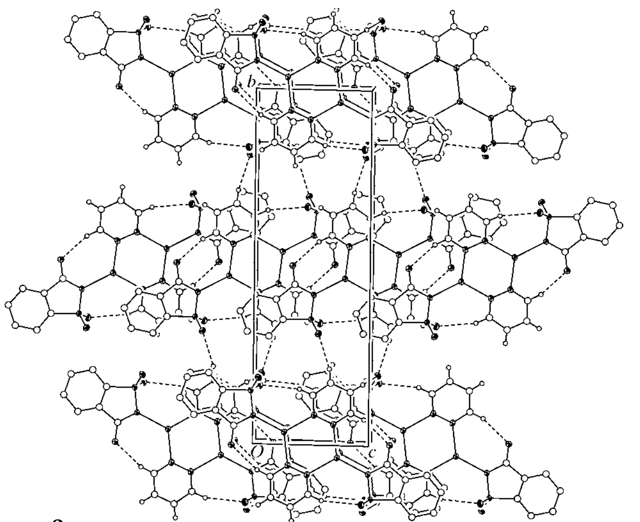

Figure 2
The packing of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines and benzene H atoms have been omitted.

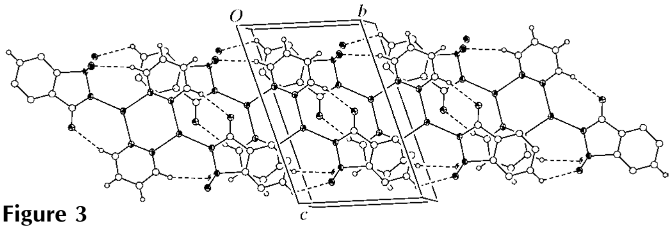

Figure 3
The packing of (II), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines and benzene H atoms not involved in hydrogen bonding have been omitted.

The molecular packing in (I) and (II) is shown in Figs. 2 and 3. The most obvious difference between the two polymorphs is clearly seen in their intermolecular interactions (Tables 2 and 4). In the monoclinic polymorph, (I), two types of interactions (π–π and C—H$\cdots$O) stabilize the structure. There are two aromatic π–π stacking interactions between the closely associated pairs of sac and pydz aromatic rings [$Cg1\cdots Cg1^{viii}$ = 3.6955 Å and $Cg1\cdots Cg1^{ix}$ = 3.8277 Å; symmetry codes: (viii) $-x+2, -y, -z+2$; (ix) $-x+1, -y, -z$], leading to two-dimensional layers, which are further crosslinked by two weak C—H$\cdots$O interactions (Fig. 2). Although the C—H$\cdots$O interactions in (II) are similar to those in (I), (II) also exhibits a π–π interaction between the aromatic rings [$Cg1\cdots Cg1^{x}$ = 3.7008 Å; symmetry code: (x) $-x+1, -y+1, -z+1$], a C—H$\cdots\pi$ interaction [C10—H10$\cdots Cg^{ii}$ = 3.2755 Å; symmetry code: (ii) $-x+2, -y+1, -z+1$], and a $\pi\cdots M$ interaction between the aromatic ring of the sac ligand and the silver(I) ion [$Cg\cdots Ag^{xi}$ = 3.879 Å; symmetry code: (xi) $x, y-1, z$]. These extra weak intermolecular interactions help stabilize the triclinic polymorphic structure.

Experimental

Nasac·2H$_2$O (0.24 g, 1 mmol) was added to a solution of AgNO$_3$ (0.17 g, 1 mmol) in water (5 ml), and the solution immediately became milky. The white precipitate was dissolved in acetonitrile (15 ml), and pydz (0.08 g, 1 mmol) was added dropwise to the solution, which was then allowed to stand in darkness at room temperature. Colourless crystals of both the monoclinic and the triclinic forms were obtained after four days (yield 94%). IR (KBr, cm^{-1}): ν(C=O) 1651; ν_{as}(S=O) 1286, 1257; ν_s(S=O) 1151.

Polymorph (I)

Crystal data

[Ag$_2$(C$_7$H$_4$NO$_3$S)$_2$(C$_4$H$_4$N$_2$)$_2$]
M_r = 740.27
Monoclinic, $P2_1/n$
a = 7.2388 (5) Å
b = 22.3068 (11) Å
c = 7.7746 (5) Å
β = 108.884 (5)°
V = 1187.83 (13) Å^3
Z = 2
D_x = 2.070 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15455 reflections
θ = 1.8–27.3°
μ = 1.88 mm^{-1}
T = 100 (2) K
Prismatic plate, colourless
0.42 × 0.28 × 0.17 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.552, T_{max} = 0.741
15455 measured reflections
2602 independent reflections
2458 reflections with $I > 2\sigma(I)$
R_{int} = 0.086
θ_{max} = 27.1°
$h = -9 \rightarrow 9$
$k = -28 \rightarrow 28$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.063
S = 1.10
2602 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.2187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.85 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—Ag1	2.2099 (18)	N3—Ag1^i	2.2632 (19)
N2—Ag1	2.276 (2)		
N1—Ag1—N2	119.82 (7)	N3^i—Ag1—N2	117.48 (7)
N1—Ag1—N3^i	121.97 (7)		

Symmetry code: (i) $-x+1, -y+1, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$O3	0.93	2.36	3.245 (3)	160
C9—H9$\cdots$O2^{ii}	0.93	2.44	3.101 (3)	128
C10—H10$\cdots$O2^{iii}	0.93	2.37	3.199 (3)	148
C11—H11$\cdots$O1^i	0.93	2.53	3.423 (3)	162

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

Polymorph (II)

Crystal data

[Ag$_2$(C$_7$H$_4$NO$_3$S)$_2$(C$_4$H$_4$N$_2$)$_2$]
M_r = 740.27
Triclinic, $P\overline{1}$
a = 7.3231 (8) Å
b = 7.7516 (9) Å
c = 11.5389 (14) Å
α = 73.090 (9)°
β = 83.087 (10)°
γ = 71.148 (9)°
V = 592.82 (12) Å^3
Z = 1
D_x = 2.074 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10253 reflections
θ = 2.9–28.0°
μ = 1.88 mm^{-1}
T = 100 (2) K
Prismatic stick, colourless
0.60 × 0.51 × 0.33 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
$T_{\rm min} = 0.368$, $T_{\rm max} = 0.579$
10253 measured reflections
2737 independent reflections
2650 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.099$
$\theta_{\rm max} = 27.6°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.066$
$S = 1.08$
2320 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_{\rm o}^2) + (0.03P)^2 + 0.5506P]$ where $P = (F_{\rm o}^2 + 2F_{\rm c}^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.74$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.19$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—Ag1	2.206 (2)	N3—Ag1$^{\rm iv}$	2.261 (2)
N2—Ag1	2.270 (2)		
N1—Ag1—N2	119.53 (8)	N3$^{\rm iv}$—Ag1—N2	117.54 (8)
N1—Ag1—N3$^{\rm iv}$	122.52 (9)		

Symmetry code: (iv) $-x+1, -y, -z+1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$O1$^{\rm v}$	0.93	2.58	3.163 (3)	121
C8—H8$\cdots$O3	0.93	2.35	3.236 (3)	160
C9—H9$\cdots$O1$^{\rm vi}$	0.93	2.47	3.152 (3)	131
C10—H10$\cdots$O1$^{\rm vii}$	0.93	2.41	3.203 (4)	143
C11—H11$\cdots$O2$^{\rm iv}$	0.93	2.52	3.410 (3)	161

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

All H atoms were refined with a riding model, with C—H distances of 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1419). Services for accessing these data are described at the back of the journal.

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