Crystal and Molecular Structures of Silver N^1-(3-Pyridyl)sulphanilamide

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The *X*-ray crystal structure analysis of the 1 : 1 title complex is reported. Two structures exist: an α-polymorph, orthorhombic, space group *Pbca* with $Z = 8$, and a β-polymorph, monoclinic, space group $P2_1/c$ with $Z = 4$. Both structures have been solved from visually estimated data by heavy-atom methods and refined by least squares to *R* 9.1 and 11.0% respectively (1 351 and 1 254 observed reflections). The silver co-ordinations for both polymorphs are similar. Each silver atom is involved in approximately linear co-ordination between two pyridylsulphanilamide molecules [α, Ag–N 2.25, 2.30 Å; β, 2.16, 2.19 Å], and two weaker Ag–O interactions in the range 2.82—2.96 Å. There is evidence for hydrogen bonding in the α-, but not the β-form. Molecular dimensions in the two polymorphs are similar and related to those of silver sulphadiazine and sulphonamide structures except for short S–O bonds in the β-form. The two polymorphic forms differ in the manner of packing the molecules in space.

THE present work was undertaken following the determination of the structure of silver sulphadiazine [1] which was shown to involve an approximately tetrahedrally co-ordinated silver atom from pyrimidine and sulphonamide nitrogen atoms and sulphamide oxygen.

The silver ' salt ' of N^1-(3-pyridyl)sulphanilamide is of interest as it reduces the possibility of intramolecular bonding between the heterocyclic nitrogen and other donor atoms with the silver atom, and one might expect a more simple structure to result.

The physical properties of silver N^1-(3-pyridyl)sulphanilamide resemble those of silver sulphadiazine (*i.e.* a light-stable compound insoluble in common solvents but soluble in ammonia solutions or nitric acid, presumably with decomposition of the complex). The i.r. spectrum of the complex also shows a similar relationship to that of the parent sulphonamide, as does that of silver sulphadiazine to that of sulphadiazine,[2] although the i.r. spectra do not enable characterisation of these complexes.

EXPERIMENTAL

Silver N^1-(3-pyridyl)sulphanilamide was prepared by mixing one equivalent of silver nitrate with one equivalent of the sodiums salt of N^1-(3-pyridyl)sulphanilamide. The precipitated silver N^1-(3-pyridyl)sulphanilamide was washed with water and dried. Crystals were prepared by slow room-temperature evaporation of the solution in 10% ammonia. The α-form crystals were well-formed pale brown equidimensional orthorhombic crystals. Those of the predominating β-form were poorly formed, pale brown, elongated monoclinic plates, twinned on planes parallel to the *b* axis.

Crystal Data.—(*a*) *α-Polymorph.* $C_{11}H_{10}AgN_3O_2S$, $M = 356.15$. Orthorhombic, $a = 14.33(1)$, $b = 10.25(1)$, $c = 17.13(2)$ Å, $U = 2\,515$ Å^3, $D_m = 1.87$, $Z = 8$, $D_c = 1.88$ g cm^{-3}, $F(000) = 1\,408$. Space group *Pbca* (D_{2h}^{15} No. 61). Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 151 cm^{-1}.

(*b*) *β-Polymorph.* $C_{11}H_{10}AgN_3O_2S$, $M = 356.15$. Monoclinic, $a = 7.518(7)$, $b = 6.713(6)$, $c = 26.19(2)$ Å, $\beta = 103.1(1)°$, $U = 1\,287$ Å^3, $D_m = 1.83$, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000) = 704$. Space group $P2_1/c$ (C_{2h}^5, No. 14). Cu-K_α radiation; μ(Cu-K_α) = 148 cm^{-1}.

Space group and unit-cell dimensions were found by use of Stoë Weissenberg and Precession-Retigraph cameras. An α-form crystal (0.2 × 0.1 × 0.1 mm) was used for the layers 0—12 *kl*, and a β-form crystal (0.2 × 0.1 × 0.15 mm) for layers *h*0*l*—*h*4*l*. Visually-estimated *X*-ray intensity data from multiple-film equi-film equi-inclination Weissenberg photographs were corrected for absorption, Lorentz, and polarisation effects. For the α-polymorph, 2 050 reflections were observed of which 1 351 had measurable intensities greater than zero. For the β-polymorph 1 254 non-zero intensities were measured from an observed total of 1 887.

[1] D. S. Cook and M. F. Turner, *J.C.S. Perkin II*, 1975, 1021.
[2] M. F. Turner, unpublished data.

TABLE 1

Final atomic co-ordinates and thermal parameters * (× 10^4)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(*a*) For α-polymorph									
Ag	1 613(1)	2 083(1)	706(1)	38(2)	92(1)	26(2)	6(5)	0(1)	13(2)
S	3 581(3)	767(3)	1 017(2)	36(2)	51(3)	28(2)	6(4)	0(2)	10(3)
O(1)	2 875(7)	393(12)	1 599(7)	52(6)	78(10)	30(3)	0(15)	8(8)	11(9)
O(2)	3 897(7)	−262(12)	519(7)	46(5)	74(12)	29(5)	2(13)	−20(7)	−19(10)
N(1)	3 170(9)	1 931(18)	533(5)	24(8)	127(14)	22(4)	28(17)	18(10)	−16(12)
C(2)	3 664(10)	2 686(16)	19(6)	54(9)	93(16)	25(5)	−2(14)	8(8)	−2(14)
C(3)	4 584(10)	2 463(18)	−204(8)	34(8)	65(10)	14(6)	−18(18)	−4(7)	−12(14)
N(4)	5 038(11)	3 296(19)	−651(8)	54(11)	69(12)	52(7)	5(19)	17(12)	−44(18)
C(5)	4 696(9)	4 293(14)	−974(9)	48(12)	74(20)	45(6)	14(20)	−9(11)	30(18)
C(6)	3 748(11)	4 556(17)	−827(10)	41(8)	92(15)	37(8)	17(22)	20(12)	41(16)
C(7)	3 193(12)	3 809(18)	−350(8)	62(10)	96(16)	64(5)	−3(21)	2(13)	21(19)
C(8)	4 594(13)	1 340(19)	1 499(9)	48(10)	47(16)	48(9)	−31(19)	0(10)	−18(17)
C(9)	5 432(12)	577(15)	1 483(8)	70(13)	115(17)	34(8)	32(24)	16(12)	22(15)
C(10)	6 221(14)	1 119(20)	1 870(7)	51(7)	102(15)	32(6)	19(18)	−31(11)	13(12)
C(11)	6 217(12)	2 292(17)	2 215(8)	45(9)	88(19)	40(5)	−28(22)	−9(11)	21(15)
C(12)	5 427(11)	2 978(18)	2 237(9)	42(10)	89(12)	29(7)	−8(21)	3(13)	−14(17)
C(13)	4 537(12)	2 538(15)	1 918(10)	61(11)	61(14)	32(6)	−7(21)	3(8)	−20(11)
N(14)	7 082(12)	2 775(17)	2 559(10)	59(9)	142(21)	28(7)	−26(23)	−15(11)	−11(18)
(*b*) For β-polymorph									
Ag	6 970(2)	7 681(3)	4 881(6)	113(4)	148(7)	13(1)	−13(8)	15(2)	−4(2)
S	3 424(7)	8 707(10)	4 051(4)	140(8)	113(14)	12(1)	23(21)	17(7)	0(5)
O(1)	5 021(18)	8 786(27)	3 861(6)	117(35)	210(70)	14(2)	−80(17)	11(12)	−3(21)
O(2)	2 550(20)	10 553(26)	4 061(7)	173(29)	131(52)	14(3)	−94(41)	−8(12)	15(17)
N(1)	4 040(16)	7 672(29)	4 610(6)	62(19)	52(48)	9(4)	8(32)	−5(12)	14(27)
C(2)	2 896(17)	7 356(47)	4 937(7)	14(16)	320(78)	8(3)	−42(50)	5(9)	11(14)
C(3)	917(26)	7 698(43)	4 832(8)	155(32)	135(97)	21(4)	−210(96)	36(17)	41(31)
N(4)	−59(20)	7 414(36)	5 137(6)	94(22)	232(59)	10(3)	91(74)	7(14)	−29(32)
C(5)	583(35)	6 829(37)	5 616(9)	240(71)	21(58)	16(5)	−112(82)	11(12)	−17(17)
C(6)	2 533(33)	6 550(42)	5 781(10)	151(40)	261(102)	18(4)	31(42)	26(19)	−24(21)
C(7)	3 643(34)	6 814(38)	5 450(10)	240(42)	114(92)	14(4)	−82(61)	24(20)	41(31)
C(8)	1807(25)	7 154(41)	3 627(9)	104(31)	214(91)	11(3)	−62(64)	18(17)	17(29)
C(9)	2 429(35)	5 421(44)	3 496(9)	224(56)	265(106)	12(4)	−83(72)	11(22)	35(23)
C(10)	1 065(37)	4 254(38)	3 151(9)	277(61)	79(78)	15(10)	−143(103)	60(29)	14(28)
C(11)	−762(34)	4 930(42)	2 968(10)	252(38)	192(103)	15(3)	−85(77)	42(27)	20(22)
C(12)	−1 361(30)	6 701(34)	3 119(9)	149(42)	126(92)	15(12)	14(49)	45(14)	5(18)
C(13)	−29(26)	7 932(37)	3 481(8)	119(31)	148(86)	13(4)	27(48)	27(21)	41(29)
N(14)	−2 063(29)	3 583(36)	2 644(9)	230(51)	162(82)	17(3)	−117(74)	19(17)	33(26)

* Anisotropic temperature factors (× 10^4) defined by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Solution and Refinement of the Structures.—The structures were both determined by the heavy-atom method, that of the β-polymorph first. Fourier syntheses of electron density, phased on silver positions from Patterson syntheses, revealed all the non-hydrogen atom positions for both α- and β-polymorphs. Refinements were by least-squares with the block-diagonal approximation and weighting scheme $\sqrt{w} = F^*/F_o$ for $|F_o| > F^*$ and $\sqrt{w} = F_o/F^*$ for $|F_o| < F^*$ with $F^* = 25$ e. Unobserved reflections were computed throughout but excluded from the refinement. Hydrogen atoms were later introduced at calculated positions, assuming C–H 1.04 Å, but were not refined. Five isotropic and two anisotropic refinement cycles gave R 9.1% for 1 351 non-zero observed reflections for the α-polymorph. Four isotropic and two anisotropic refinement cycles gave R 11.0% for 1 254 non-zero observed reflections for the β-polymorph. The final parameter shifts were not $>\frac{1}{3}\sigma$. The lower accuracy in the case of the β-polymorph is due to the poor crystals available for the analysis. Table 1 lists final atomic co-ordinates and thermal parameters for the α- and β-polymorphs respectively.*

DISCUSSION

Molecular Structures.—Figure 1 shows the pyridylsulphanilamide moiety and the atom numbering. Table 2 lists intermolecular contact distances and angles. Related molecules in the two structures have been labelled where possible to emphasise the similar silve co-ordinations found for the two structures. Each silver atom chelates one pyridylsulphanilamide molecule *via* N(1) and O(1), and bonds to two others *via* N(4) and O(2). The primary cohesive feature is a near-linear

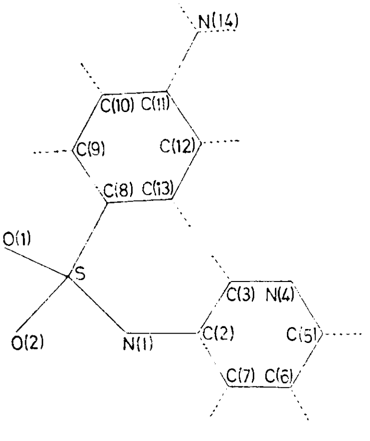

FIGURE 1 Pyridylsulphanilamide moiety of silver N^1-(3-pyridyl)sulphanilamide

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21732. (3pp), See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

N(1)–Ag–N(4) co-ordination parallel to the *a* axes for both structures. The Ag–N distances for the α- [2.25(1) and 2.30(1) Å] are longer than for the β-polymorph [2.16(1) and 2.19(1) Å], and are to be compared with the Ag–N distances of [2.24(1) and 2.45(1) Å] for silver sulphadiazine [1] and values between 2.1 and 2.4 Å [3-8] for compounds showing Ag–N bonding. The Ag–O(1) and Ag–O(2) distances [2.82(1)—2.96(1) Å] represent very weak interactions compared with other reported values.[1,5,7,9-11]

The main structural feature which differentiates the α- and β-polymorphs is the disposition of the molecules at each end of the N(1)–Ag–N(4) bond (Figure 2). For the α-form the molecules, and especially the terminal amine groups, point in opposite directions, whilst rotation of one molecule about the N(1)–Ag–N(4) direction by 180° gives the β-form, with the amine groups pointing in the same direction. A foreshortened pseudo-mono-

TABLE 2

Intermolecular contacts [distances (Å), angles (°)]

(*a*) α-Polymorph

(i) Ag–X distances

Ag–N(1)	2.25(1)	Ag–O(1)	2.93(1)
Ag–N(4$^{\mathrm{II}}$)	2.30(1)	Ag–O(2$^{\mathrm{VII}}$)	2.82(1)

(ii) X–Ag–X angles

N(1)–Ag–N(4$^{\mathrm{II}}$)	163(1)	O(1)–Ag–O(2$^{\mathrm{VII}}$)	141(1)
N(1)–Ag–O(1)	55(1)	O(1)–Ag–N(4$^{\mathrm{II}}$)	121(1)
N(1)–Ag–O(2$^{\mathrm{VII}}$)	107(1)	N(4$^{\mathrm{II}}$)–Ag–O(2$^{\mathrm{VII}}$)	85(1)

(iii) Ag–X–X angles

Ag–O(1)–S	86(1)	Ag–N(1)–C(2)	125(1)
Ag–O(2$^{\mathrm{VII}}$)–S$^{\mathrm{VII}}$	124(1)	Ag–N(4$^{\mathrm{II}}$)–C(3$^{\mathrm{II}}$)	115(1)
Ag–N(1)–S	110(1)	Ag–N(4$^{\mathrm{II}}$)–C(5$^{\mathrm{II}}$)	121(1)

(iv) Hydrogen-bond distances

O(1) · · · N(14$^{\mathrm{IV}}$)	3.04(2)	O(1) · · · N(14$^{\mathrm{IX}}$)	3.06(2)

(v) Hydrogen-bond angles

S–O(1)–N(14$^{\mathrm{IV}}$)	112(1)	O(1)–N(14$^{\mathrm{IV}}$)–C(11$^{\mathrm{IV}}$)	104(1)
S–O(1)–N(14$^{\mathrm{IX}}$)	121(1)	O(1)–N(14$^{\mathrm{IX}}$)–C(11$^{\mathrm{IX}}$)	119(1)

(vi) Other short contacts <3.8

Ag · · · X

Ag · · · C(3$^{\mathrm{II}}$)	3.08(1)	Ag · · · C(2)	3.23(1)
Ag · · · N(14$^{\mathrm{IV}}$)	3.13(1)	Ag · · · C(7)	3.39(1)
Ag · · · C(5$^{\mathrm{II}}$)	3.14(1)	Ag · · · C(11$^{\mathrm{IV}}$)	3.61(1)
Ag · · · S	3.17(1)	Ag · · · C(6$^{\mathrm{VI}}$)	3.77(1)

Others

N(4) · · · C(5$^{\mathrm{III}}$)	3.78(2)	O(2) · · · O(2$^{\mathrm{V}}$)	3.69(2)
N(4) · · · C(6$^{\mathrm{III}}$)	3.79(2)	O(2) · · · C(9$^{\mathrm{V}}$)	3.57(2)
O(1) · · · C(10$^{\mathrm{IV}}$)	3.58(2)	O(2) · · · C(3$^{\mathrm{V}}$)	3.20(2)
O(1) · · · C(11$^{\mathrm{IV}}$)	3.69(2)	O(2) · · · N(4$^{\mathrm{V}}$)	3.48(2)
N(1) · · · N(14$^{\mathrm{IV}}$)	3.74(2)	O(2) · · · C(7$^{\mathrm{VI}}$)	3.47(2)
C(13) · · · N(14$^{\mathrm{IV}}$)	3.61(2)	C(12) · · · C(9$^{\mathrm{VIII}}$)	3.67(2)

Roman numeral superscripts refer to the molecules associated with the following equivalent positions:

II	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$	VI	$\frac{1}{2}-x, -\frac{1}{2}+y, z$
III	$1-x, 1-y, -z$	VII	$\frac{1}{2}-x, \frac{1}{2}+y, z$
IV	$-\frac{1}{2}+x, y, \frac{1}{2}-z$	VIII	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
V	$1-x, -y, -z$	IX	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$

(*b*) β-Polymorph

(i) Ag–X distances

Ag–N(1)	2.16(1)	Ag–O(1)	2.83(1)
Ag–N(4$^{\mathrm{II}}$)	2.19(1)	Ag–O(2$^{\mathrm{VII}}$)	2.96(1)

(ii) X–Ag–X angles

N(1)–Ag–N(4$^{\mathrm{II}}$)	175(1)	O(1)–Ag–O(2$^{\mathrm{VII}}$)	134(1)
N(1)–Ag–O(1)	55(1)	O(1)–Ag–N(4$^{\mathrm{II}}$)	125(1)
N(1)–Ag–O(2$^{\mathrm{VII}}$)	102(1)	N(4$^{\mathrm{II}}$)–Ag–O(2$^{\mathrm{VII}}$)	82(1)

(iii) Ag–X–X angles

Ag–O(1)–S	87(1)	Ag–N(1)–C(2)	123(1)
Ag–O(2$^{\mathrm{VII}}$)–S$^{\mathrm{VII}}$	114(1)	Ag–N(4$^{\mathrm{II}}$)–C(3$^{\mathrm{II}}$)	121(1)
Ag–N(1)–S	111(1)	Ag–N(4$^{\mathrm{II}}$)–C(5$^{\mathrm{II}}$)	116(1)

TABLE 2 (*Continued*)

(iv) Other short contacts <3.8

Ag · · · X

Ag · · · C(3$^{\mathrm{II}}$)	3.00(2)	Ag · · · C(2$^{\mathrm{VII}}$)	3.36(3)
Ag · · · C(5$^{\mathrm{II}}$)	3.00(2)	Ag · · · C(6$^{\mathrm{IV}}$)	3.39(3)
Ag · · · S	3.11(1)	Ag · · · C(2$^{\mathrm{IV}}$)	3.40(3)
Ag · · · C(2)	3.11(1)	Ag · · · C(3$^{\mathrm{VII}}$)	3.50(3)
Ag · · · C(7$^{\mathrm{IV}}$)	3.14(3)	Ag · · · N(1$^{\mathrm{VII}}$)	3.55(2)
Ag · · · C(7)	3.24(3)	Ag · · · S$^{\mathrm{VII}}$	3.76(1)

Others

N(4) · · · C(3$^{\mathrm{III}}$)	3.50(3)	C(12) · · · C(10$^{\mathrm{VI}}$)	3.79(3)
C(5) · · · C(3$^{\mathrm{III}}$)	3.36(3)	C(7) · · · S$^{\mathrm{VII}}$	3.79(3)
C(5) · · · N(4$^{\mathrm{III}}$)	3.43(3)	C(6) · · · O(1$^{\mathrm{VII}}$)	3.65(3)
C(6) · · · N(4$^{\mathrm{III}}$)	3.77(3)	C(7) · · · O(1$^{\mathrm{VII}}$)	3.50(3)
N(4) · · · N(4$^{\mathrm{III}}$)	3.32(3)	C(7) · · · O(2$^{\mathrm{VII}}$)	3.38(3)
C(10) · · · C(5$^{\mathrm{III}}$)	3.78(3)	N(14) · · · C(8$^{\mathrm{VIII}}$)	3.53(3)
C(7) · · · N(1$^{\mathrm{IV}}$)	3.51(3)	N(14) · · · C(9$^{\mathrm{VIII}}$)	3.63(3)
N(4) · · · O(2$^{\mathrm{V}}$)	3.41(3)	N(14) · · · C(10$^{\mathrm{VIII}}$)	3.76(3)
C(5) · · · O(2$^{\mathrm{V}}$)	3.20(3)	N(14) · · · C(11$^{\mathrm{VIII}}$)	3.80(3)
C(3) · · · C(3$^{\mathrm{V}}$)	3.59(3)	N(14) · · · C(12$^{\mathrm{VIII}}$)	3.80(3)
N(4) · · · C(3$^{\mathrm{V}}$)	3.37(3)	N(14) · · · C(13$^{\mathrm{VIII}}$)	3.66(3)
N(4) · · · N(4$^{\mathrm{V}}$)	3.56(3)		

Roman numeral superscripts define the following equivalent positions:

II	$1+x, y, z$	VI	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
III	$-x, 1-y, 1-z$	VII	$1-x, 2-y, 1-z$
IV	$1-x, 1-y, 1-z$	VIII	$-x, -\frac{1}{2}+y, \frac{1}{2}-z$
V	$-x, 2-y, 1-z$		

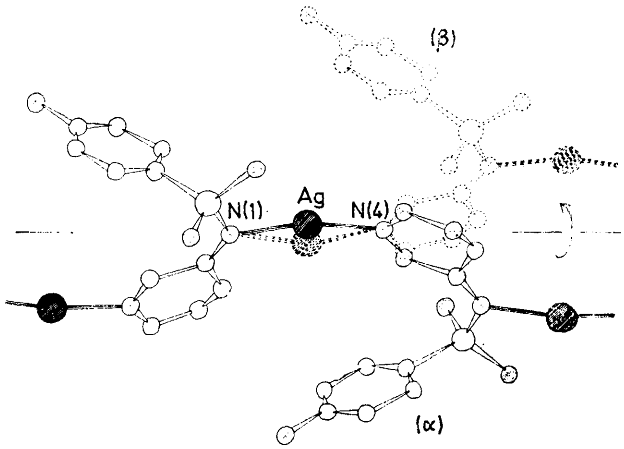

FIGURE 2 Rotation of molecule on right by 180° about N(1)–Ag–N(4) gives α- and β-configurations with molecules pointing in opposite or same directions respectively. Large shaded circles Ag, large open circle S, small open circle C, crossed circle N, dotted circle O

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clinic β-cell can be seen, however, in almost the same orientation within half the orthorhombic α-cell.

Hydrogen atoms were not located in the present analysis but the interatomic distances give strong evidence for the existence of hydrogen bonding in the α-polymorphic form, but not for the single-crystal β-form. For the α-form the terminal NH_2 group of the benzene ring is hydrogen-bonded to atoms O(1) of two separate molecules, forming lines of hydrogen-bonds parallel to the *b* axis (Figure 3). Unlike related sulphonamide structures and silver sulphadiazine,[1] oxygen atom (O2) does not participate in hydrogen bonding, and this is reflected in the lengthening of the Ag–O(1) and S–O(1) bond lengths with respect to Ag–O(2) and S–O(2). The hydrogen-bond distances [3.04(2) and 3.06(2) Å] are the same as for silver sulphadiazine.

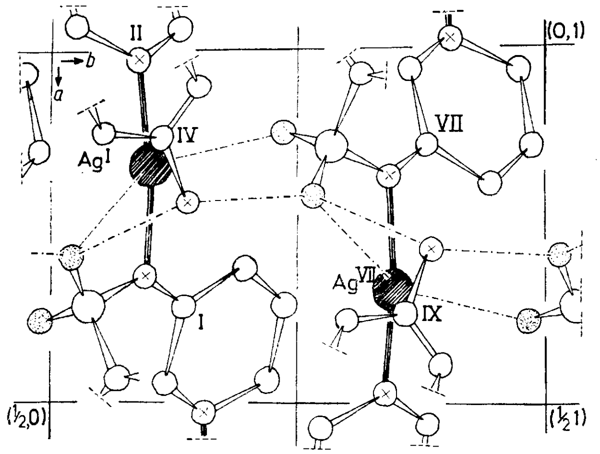

FIGURE 3 The α-polymorph viewed down the *c* axis. Ag–N interactions (triple solid lines), N–H · · · OS hydrogen bonding (heavy dot-dash lines), Ag–O interactions (light dot-dash lines). Atom identification as Figure 2; equivalent positions defined by Roman numerals as listed in Table 2 (*a*) (atoms with superscript I are at *x*, *y*, *z*)

There is no evidence for the existence of hydrogen bonding for the β-polymorph in its single-crystal form. However, most of the crystals examined were irregularly twinned with misorientation of the *a* and *c* axes, although the exact mode of twinning could not be found. It is possible that slight rotations of the molecules may occur across the twin boundaries to give hydrogen bonding between N(14) and O(1) (4.18 Å apart in the single crystal form), as in the α-form. This is supported by the fact that only weak van der Waals forces hold the ends of these molecules together in the single-crystal form.

These results confirm the type of bonding found for silver sulphadiazine where the terminal amino-group was not involved in bonding, except hydrogen bonding. The differences between the present structures and that of silver sulphadiazine appear to be caused by the position of the heterocyclic nitrogen atoms which do not allow linear co-ordination of the silver atom in silver sulphadiazine. This atom is sufficiently close to an oxygen atom of the sulphamide group to enable co-ordination with the result that there is a rigid structure and a distorted tetrahedral stereochemistry about the silver atom. For the present work the corresponding oxygen atom is not in a position to co-ordinate to the silver atom and there is a less rigid network, reflected by the higher thermal parameters and, indeed, by the presence of polymorphism, which is also exhibited by many sulphonamides.[12]

TABLE 3

Intramolecular bond distances (Å) and angles (°) for the *N*¹-(3-pyridyl)sulphanilamide moiety of the α- and β-polymorphs

(*a*) Distances

	α	β
N(1)–C(2)	1.36(2)	1.37(2)
C(2)–C(3)	1.40(3)	1.45(3)
C(3)–N(4)	1.33(2)	1.26(3)
N(4)–C(5)	1.26(2)	1.31(3)
C(5)–C(6)	1.36(3)	1.43(3)
C(6)–C(7)	1.40(3)	1.35(3)
C(7)–C(2)	1.42(3)	1.38(3)
S–N(1)	1.61(2)	1.59(2)
S–O(1)	1.47(1)	1.40(2)
S–O(2)	1.43(1)	1.40(2)
S–C(8)	1.78(2)	1.78(3)
C(8)–C(9)	1.41(3)	1.34(3)
C(9)–C(10)	1.42(3)	1.44(3)
C(10)–C(11)	1.38(3)	1.43(3)
C(11)–N(14)	1.47(3)	1.44(3)
C(11)–C(12)	1.35(3)	1.37(3)
C(12)–C(13)	1.46(3)	1.46(3)
C(13)–C(8)	1.43(2)	1.45(3)

(*b*) Angles

	α	β
O(1)–S–O(2)	115	114
O(2)–S–N(1)	111	114
C(8)–S–N(1)	108	109
O(1)–S–C(8)	110	109
O(1)–S–N(1)	108	106
O(2)–S–C(8)	105	106
S–N(1)–C(2)	126	124
N(1)–C(2)–C(7)	119	119
N(1)–C(2)–C(3)	124	125
C(7)–C(2)–C(3)	117	114
C(2)–C(3)–C(4)	120	124
C(3)–N(4)–C(5)	123	123
N(4)–C(5)–C(6)	117	117
C(5)–C(6)–C(7)	124	121
C(6)–C(7)–C(2)	116	120
S–C(8)–C(9)	120	117
S–C(8)–C(13)	116	115
C(13)–C(8)–C(9)	124	126
C(8)–C(9)–C(10)	119	116
C(9)–C(10)–C(11)	121	122
C(10)–C(11)–C(12)	121	122
C(10)–C(11)–N(14)	117	118
C(12)–C(11)–N(14)	122	119
C(11)–C(12)–C(13)	123	117
C(12)–C(13)–C(8)	116	117

Mean standard deviations for all angles involving sulphur 1°; all other angles 1.5 (α) and 2° (β)

All the remaining short intermolecular distances (<3.8 Å) due to possible weak van der Waals interactions are given in Table 2. Since there is no hydrogen bonding in the single-crystal β-form, these interactions appear to be of greater significance for the structural cohesion of the β-polymorph than for the α-polymorph.

Pyridylsulphanilamide Moiety.—Intramolecular bond

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[12] S. S. Yang and J. K. Guillory, *J. Pharm. Sci.*, 1972, **61**, 26.

lengths and angles for the α- and β-polymorphs are given in Table 3.

There is general agreement for the dimensions of the two polymorphic forms with the exception of the S–O bond distances [α, 1.47(1) and 1.43(1); β, 1.40(2) and 1.40(2) Å]. The presence of the silver atom does not appreciably modify the expected sulphonamide structure.

TABLE 4

Equations of least-squares planes in the form $lX + mY + nZ + P = 0$, where X, Y, Z are orthogonal (Å) co-ordinates having X, Y, Z along the a, b, and c * axes. Deviations (Å) of atoms from the plane are given in square brackets

Benzene plane (α): C(8)—(13), N(14), S

$$0.257X + 0.457Y - 0.852Z - 0.102 = 0$$

[C(8) 0.02, C(9) 0.01, C(10) −0.03, C(11) 0.01, C(12) 0.03, C(13) −0.04, N(14) * 0.06, S * 0.08]

Benzene plane (β): C(8)—(13), N(14), S

$$0.433X + 0.444Y - 0.785Z + 5.500 = 0$$

[C(8) 0.01, C(9) 0, C(10) −0.01, C(11) 0.01, C(12) 0, C(13) −0.01, N(14) * −0.08, S * 0.05]

Pyridine plane (α): C(2), C(3), N(4), C(5)—(7), N(1)

$$-0.281X - 0.567Y - 0.774Z + 3.052 = 0$$

[C(2) −0.03, C(3) 0.05, N(4) −0.04, C(5) 0, C(6) 0.02, C(7) −0.01, N(1) * −0.03]

Pyridine plane (β): C(2), C(3), N(4), C(5)—(7), N(1)

$$-0.065X - 0.957Y - 0.284Z + 8.277 = 0$$

[C(2) 0.01, C(3) −0.01, N(4) 0, C(5) 0.01, C(6) −0.01, C(7) 0, N(1) * 0]

Dihedral angle 71 (α), 77° (β polymorph)

* Ring-attached atoms.

The short S–O bond distances for the β-polymorph are comparable with those of sulphamide [13] but shorter than those listed for sulphonamides [14–18] or silver sulphadiazine.[1] This may be due to the lack of hydrogen bonding in this polymorph and to the very weak Ag–O interactions compared to those of silver sulphadiazine. Also the S–C(8) and N(14)–C(11) bond distances for both polymorphs are no longer than expected, indicating a less quinoidal nature than for similar structures and this would help to shorten the S–O bond distances. The stereochemistry about the sulphur atom is as expected approximately tetrahedral. The N(1)–C(2) bond distance for both polymorphs is much shorter than for silver sulphadiazine. This indicates that there is some contribution from the imide form which some of the sulphonamides, particularly sulphapyridine, are known to exhibit.

The other features of both polymorphs are very similar to those reported for silver sulphadiazine.

Least-squares planes were derived for the benzene and pyridyl rings and the ring attached atoms. The results (Table 4) show that both ring-attached atoms are significantly displaced from the plane of the benzene ring for each polymorph. In silver sulphadiazine only the sulphur atom was displaced from the ring plane, but in β-sulphanilamide [15] both ring-attached nitrogen and sulphur atoms are displaced from the plane. The dihedral angle between the planes of the two rings is 71 for the α- and 77° for the β-polymorph.

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