Lewis-base Adducts of Group 1B Metal(I) Compounds. Part 5.[1] Synthesis and Crystal Structures * of Adducts of Silver(I) Thiocyanate with 2- and 3-Methylpyridine, 2,6-Dimethylpyridine, and Quinoline

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The crystal structures of the title compounds [{Ag(SCN)L}$_n$] [L = 2-methylpyridine (1), 3-methylpyridine (2), or 2,6-dimethylpyridine (3)] and [{Ag(SCN)L$_2$}$_n$] [L = quinoline (4)] have been established by single-crystal *X*-ray diffraction methods at 295(1) K and refined by least squares to residuals of 0.061, 0.046, 0.055, and 0.031 for 1 139, 1 478, 956, and 2 399 independent 'observed' reflections respectively. Crystals of (1) are orthorhombic, space group $Pn2_1a$, with a = 18.350(5), b = 11.209(3), c = 4.180(1) Å, and Z = 4; the structure is an infinite two-dimensional polymer parallel to bc, with silver atoms pseudo-tetrahedrally four-co-ordinated by the sulphur and nitrogen atoms of bridging thiocyanate groups [Ag–S, 2.552(3) and 2.637(3); Ag–N, 2.27(1) Å] and by the 2-methylpyridine [Ag–N, 2.34(1) Å]. There is some disorder. Crystals of (2) are orthorhombic, space group $Pbca$, with a = 18.055(8), b = 11.385(5), c = 8.404(4) Å, and Z = 8. The structure is an infinite two-dimensional polymer parallel to bc with silver atoms pseudo-tetrahedrally four-co-ordinated by the sulphur and nitrogen atoms of the bridging thiocyanate groups [Ag–S, 2.578(2) and 2.615(2); Ag–N, 2.293(5) Å] and by the 3-methylpyridine [Ag–N, 2.331(5) Å]. Crystals of (3) are monoclinic, space group $P2_1/c$, with a = 8.481(3), b = 8.102(2), c = 13.676(7) Å, β = 97.41(3)°, and Z = 4. The structure is a one-dimensional polymer generated by the 2_1 screw along b; the silver atom is three-co-ordinated by sulphur and nitrogen atoms of the bridging thiocyanate ligand [Ag–S, 2.474(3); Ag–N, 2.28(1) Å] and by the 2,6-dimethylpyridine ligand [Ag–N, 2.275(8) Å]. The change in co-ordination number in the latter complex is attributable to the increased steric bulk of the 2,6-dimethylpyridine ligand compared to the monosubstituted analogues. Crystals of (4) are orthorhombic, space group $P2_12_12_1$, with a = 15.977(4), b = 13.544(4), c = 8.009(2) Å, and Z = 4. The structure is the first established for a silver halide/pseudo-halide–nitrogen base complex with 1 : 2 stoicheiometry. It is a one-dimensional polymer generated by the 2_1 screw along c, with four-co-ordinate pseudo-tetrahedral silver atoms linked by S,N-bridging thiocyanate groups [Ag–S, 2.495(1); Ag–N, 2.332(5) Å]. The remaining two co-ordination sites of the silver are filled by quinoline nitrogen atoms [Ag–N, 2.364(3) and 2.361(4) Å].

As part of our series of structural studies of adducts of silver(I) halides with nitrogen bases, we have explored the nature of the complexes obtained when pseudohalogen species, in particular the thiocyanate ion, are employed rather than the halide. We find that 1 : 1 silver(I) thiocyanate–base complexes may be obtained by recrystallization of silver(I) thiocyanate from neat 2- and 3-methylpyridine (2Me-py and 3Me-py) and 2,6-dimethylpyridine (2,6Me$_2$-py); a 1 : 2 complex has been obtained with quinoline (quin) and is also reported.

The combination of bases chosen is designed to provide information about situations in which pyridine ligands, unsubstituted, monosubstituted, and disubstituted in the 2- and 6-positions are incorporated, in the expectation that the successive change in effective steric bulk of the ligand will lead to a variety of structural types.

All specimens were mounted in capillaries.

Experimental

Crystallography.—General details are given in the preceding paper.[1]

Crystal data. [Ag(SCN)(2Me-py)] (1). $C_7H_7AgN_2S$, M = 259.1, orthorhombic, space group $Pn2_1a$ (variant of C_{2v}^9, no. 33), a = 18.350(5), b = 11.209(3), c = 4.180(1) Å, U = 860(1) Å^3, D_c = 2.00 g cm^{-3}, Z = 4, $F(000)$ = 504, μ_{Mo} = 24.5 cm^{-1}. Specimen: 0.45 × 0.25 × 0.28 mm. $2\theta_{max.}$ = 65°; N,N_0 = 1 619, 1 139; R,R' = 0.061, 0.079 (preferred chirality).

[Ag(SCN)(3Me-py)] (2). $C_7H_7AgN_2S$, M = 259.1, orthorhombic, space group $Pbca$ (D_{2h}^{15}, no. 61), a = 18.055(8), b = 11.385(5), c = 8.404(4) Å, U = 1 728(1) Å^3, D_c = 1.99 g cm^{-3}, Z = 8, $F(000)$ = 1 008, μ_{Mo} = 24.4 cm^{-1}. Specimen: 0.23 × 0.62 × 0.12 mm. $2\theta_{max.}$ = 55°; N,N_0 = 1 907, 1 478; R,R' = 0.046, 0.056.

[Ag(SCN)(2,6Me$_2$-py)] (3). $C_8H_9AgN_2S$, M = 273.1, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 8.481(3), b = 8.102(2), c = 13.676(7) Å, β = 97.41(3)°, U = 932(1) Å^3, D_c = 1.95 g cm^{-3}, Z = 4, $F(000)$ = 536, μ_{Mo} = 22.7 cm^{-1}. Specimen: 0.25 × 0.25 × 0.07 mm. $2\theta_{max.}$ = 50°; N,N_0 = 1 581, 956; R,R' = 0.055, 0.058.

[Ag(SCN)(quin)$_2$] (4). $C_{19}H_{14}AgN_3S$, M = 424.3, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), a = 15.977(4), b = 13.544(4), c = 8.009(2) Å, U = 1 733(1) Å^3, D_c = 1.63 g cm^{-3}, Z = 4, $F(000)$ = 848, μ_{Mo} = 12.6 cm^{-1}. Specimen: 0.28 × 0.22 × 0.50 mm. $2\theta_{max.}$ = 60°; N,N_0 = 2 871, 2 399; R,R' = 0.031, 0.039 (preferred chirality).

Abnormal features. In complex (1) some disorder was observed, possibly due to stacking faults. The largest peak (X) in a difference map obtained after refinement of the basic structure was close to the silver atom (Ag · · · X, 1.77 Å) and was refined as a fractionally populated silver atom. Other peaks observed in the difference map were smaller in magnitude and were left unmodelled. A number of reflections seemingly badly in error due to extinction were deleted from the refinement; the origin of the anomaly may be the above, however.

Non-hydrogen atom labelling in the ligand is as shown

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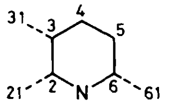
* *Supplementary data available* (No. SUP 23771, 35 pp.): structure factors, thermal parameters, hydrogen parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

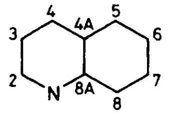
Table 1. Non-hydrogen atomic co-ordinates for complexes (1)—(3)

	(1)[a]			(2)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ag	0.216 48(4)	0[b]	0.094 0(3)	0.075 64(3)	0.152 77(3)	0.194 94(5)
Thiocyanate						
S	0.294 7(2)	−0.049 2(3)	−0.393 5(8)	0.017 56(9)	0.246 2(1)	−0.055 0(2)
C	0.298 4(6)	−0.195 3(10)	−0.403 1(30)	−0.021 8(3)	0.125 7(4)	−0.128 9(7)
N	0.302 0(7)	−0.299 5(9)	−0.410 8(30)	−0.049 9(3)	0.044 1(4)	−0.179 9(6)
Pyridine ligand						
N(1)	0.098 7(6)	−0.070 0(9)	0.204 0(30)	0.203 6(3)	0.152 5(4)	0.232 1(6)
C(2)	0.074 8(6)	−0.175 6(10)	0.119 0(26)	0.246 0(3)	0.068 6(5)	0.167 2(6)
C(3)	0.003 6(7)	−0.212 0(13)	0.188 0(36)	0.321 3(3)	0.059 4(5)	0.190 2(6)
C(4)	−0.042 1(7)	−0.136 2(17)	0.354 4(36)	0.354 2(4)	0.139 6(6)	0.288 3(7)
C(5)	−0.016 7(8)	−0.029 0(16)	0.440 2(40)	0.310 9(4)	0.226 9(7)	0.355 6(9)
C(6)	0.054 8(6)	0.001 9(18)	0.367 0(28)	0.236 3(3)	0.230 6(6)	0.323 8(7)
C(21,31)	0.127 5(7)	−0.254 9(13)	−0.057 3(42)	0.366 5(4)	−0.031 8(6)	0.107 3(10)

	(3)		
Atom	*x*	*y*	*z*
Ag	0.171 6(1)	0.052 7(1)	0.134 1(1)
Thiocyanate			
S	−0.030 2(4)	0.302 8(4)	0.434 2(2)
C	0.040 3(12)	0.222 8(13)	0.336 8(10)
N	0.088 8(12)	0.164 3(13)	0.271 9(9)
Pyridine ligand			
N(1)	0.415 4(9)	0.161 2(10)	0.121 1(6)
C(2)	0.434 0(13)	0.324 7(13)	0.117 7(8)
C(3)	0.583 8(13)	0.394 8(12)	0.119 8(8)
C(4)	0.715 4(13)	0.294 6(17)	0.130 3(9)
C(5)	0.696 1(13)	0.128 2(16)	0.133 1(9)
C(6)	0.542 9(11)	0.061 0(14)	0.129 0(8)
C(21)	0.286 7(13)	0.429 9(14)	0.107 4(9)
C(61)	0.518 2(13)	−0.122 5(13)	0.129 6(9)

[a] Also: Ag[population 0.149(8)]: 0.215 2(5), 0.000 9(20), −0.329 3(33). [b] Defines origin.





above: hydrogen-atom labelling follows that of the parent carbon, suffixed A, B, C in the case of methyl hydrogens.

Tables 1 and 2 give the atomic co-ordinates of the complexes, Table 3 the silver environments and Tables 4 and 5 the ligand geometries.

Discussion

[{Ag(SCN)(2Me-py)}$_n$] (1).—The structure determination confirms the assignment of 1 : 1 stoicheiometry for the silver(I) thiocyanate–2Me-py adduct, one formula unit of which comprises the asymmetric unit of the structure. The nature of the structure is best appreciated by consideration of Figure 1; the structure is shown for a number of unit cells in projection down *a*, and is generated by a combination of unit translations and glide planes as an infinite polymer in the *bc* plane. One such polymeric layer is found for every unit dimension in *a*. The shortest repeat distance in the polymer is the *c* translation, successive silver atoms in this short dimension [4.180(1) Å] being bridged by the sulphur atoms of the thiocyanate groups approximately midway between them at distances of 2.552(3) and 2.637(3) Å (Table 3), and occupying two of the four silver co-ordination sites. The angle S–Ag–S is 107.3(1)° while Ag–S–Ag is also 107.3(1)°. The remaining C–S–Ag angles about the sulphur atom are 105.0(4) and 102.2(4)° so that the sulphur-atom geometry is effectively tetrahedral with one co-ordination site vacant. A third co-ordination site about the silver atom is filled by the pyridine base [Ag–N, 2.34(1) Å]. In the sequence of –S–AgN–S– units building up the array along *c* by the unit translation, all pyridine base ligands lie with their N–C(4) vectors directed outwards from the sheet in the same direction and approximately parallel to *a*, while the S–N vectors of the thiocyanate groups are also parallel to and in the same sense relative to *b*. The thiocyanate nitrogen atoms of this array bridge linearly [C–N–Ag, 168(1)°; Ag–N, 2.27(1) Å] to the fourth co-ordination sites of the silver atoms in a similar array displaced by half the cell dimension in *b* and also in *c* by the *n* glide, in consequence of which the pyridine ligands of this second sequence are directed in the opposite direction relative to *a* to those of the first array. The overall result is that strings of pyridine ligands project to one side of the polymer plane when their generator is the *c* translation and then to the other side as the second string is generated by the *n* glide. As successive polymeric planes are stacked one on top of the other up *a*, we thus find the pyridine base strings neatly interlocking with the gaps of the previous layer (see below). In view of this the postulation of stacking faults as the probable origin of the refinement anomaly seems reasonable, the postulated frac-

Table 2. Non-hydrogen atomic co-ordinates for complex (4)

Atom	*x*	*y*	*z*
Ag	0.188 12(2)	0.165 22(2)	0.080 30(4)
S	0.122 88(7)	0.062 98(9)	−0.143 9(2)
C	0.191 8(2)	−0.024 8(3)	−0.180 0(5)
N	0.236 5(3)	−0.088 5(3)	−0.206 8(6)

Quinoline ligand

	Ligand 1			Ligand 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
N(1)	0.081 8(2)	0.229 2(3)	0.254 7(4)	0.283 2(2)	0.294 1(3)	0.021 2(6)
C(2)	0.079 0(3)	0.203 9(3)	0.413 8(6)	0.332 3(3)	0.320 5(4)	0.144 1(8)
C(3)	0.018 8(3)	0.237 7(4)	0.525 2(6)	0.394 0(4)	0.394 0(5)	0.131 6(9)
C(4)	−0.042 1(3)	0.299 3(4)	0.470 1(7)	0.404 6(3)	0.439 7(4)	−0.012 2(11)
C(5)	−0.101 6(3)	0.396 1(4)	0.233 2(7)	0.359 5(4)	0.461 6(5)	−0.309 6(10)
C(6)	−0.098 6(3)	0.423 3(4)	0.071 6(8)	0.307 8(5)	0.437 3(5)	−0.434 8(10)
C(7)	−0.034 5(3)	0.385 8(4)	−0.032 5(6)	0.247 5(4)	0.363 0(5)	−0.413 2(8)
C(8)	0.023 3(3)	0.321 8(3)	0.028 3(6)	0.241 3(3)	0.314 7(4)	−0.263 5(7)
C(4A)	−0.042 2(2)	0.328 9(3)	0.302 0(5)	0.354 3(3)	0.414 9(3)	−0.152 6(8)
C(8A)	0.021 6(2)	0.292 0(3)	0.196 4(5)	0.292 8(2)	0.340 9(3)	−0.128 9(6)

Table 3. Silver atom environments for complexes (1)—(4). The first column in each matrix, *r*, is the silver–ligand distance (Å). Other entries are the angles subtended at the silver by the relevant atoms at the head of the row and column. Base ligand nitrogen atoms are italicized. Transformations of the asymmetric unit are given below the matrix to which they relate

(1)	*r*	*N(1)*	S$^{\text{i}}$	N$^{\text{ii}}$
S	2.552(3)	127.0(3)	107.3(1)	106.9(3)
N(1)	2.34(1)		105.8(3)	101.2(4)
S$^{\text{i}}$	2.637(3)			107.2(3)
N$^{\text{ii}}$	2.27(1)			

i $x, y, 1 + z$; ii $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$.

(2)	*r*	*N(1)*	S$^{\text{i}}$	N$^{\text{ii}}$
S	2.578(2)	120.8(1)	108.08(5)	106.0(1)
N(1)	2.331(5)		106.9(1)	101.9(2)
S$^{\text{i}}$	2.615(2)			113.1(1)
N$^{\text{ii}}$	2.293(5)			

i $x, \frac{1}{2} - y, \frac{1}{2} + z$; ii $\bar{x}, \bar{y}, \bar{z}$.

(3)	*r*	*N(1)*	S$^{\text{i}}$
N	2.28(1)	106.9(3)	116.8(3)
N(1)	2.275(8)		133.5(2)
S$^{\text{i}}$	2.474(3)		

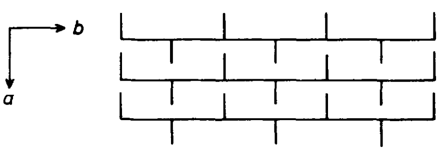
i $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$ (Σ angles = 357.2°).

(4)	*r*	*N(11)*	*N(21)*	S
N$^{\text{i}}$	2.332(5)	95.9(1)	98.3(1)	119.6(1)
N(11)	2.364(3)		108.0(1)	109.2(1)
N(21)	2.361(4)			122.3(1)
S	2.495(1)			

i $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$.

tional silver atom having *x* and *y* co-ordinates closely comparable to the major component but with a displacement in *z*.

The hexagonal two-dimensional polymeric motif is reminiscent of that observed in ammonium silver thiocyanate[2] in which silver and sulphur atoms are bridged into a puckered planar array with the out-of-plane co-ordination sites occupied by S-thiocyanate groups rather than pyridine base as is the case here. In the present structure, the hexagonal motif is elongated in one dimension by a reduction of the bridging function of the thiocyanate sulphur by the substitution of the nitrogen atom instead, so that the thiocyanate groups move into the ' plane ' of the polymer.

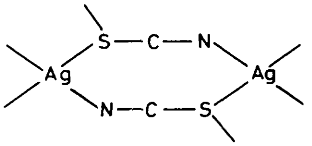


The angles Ag–N–C(2,6) at the pyridine base nitrogen are unsymmetrical [123.9(8) and 117.1(9)° respectively]. This is probably a consequence of the proximity of the methyl substituent to the neighbouring thiocyanate group, C(21) $\cdots$ S,N being 4.09(1) and 3.56(2) Å respectively.

[{Ag(SCN)(3Me-py)}$_n$] (2).—The structure determination confirms the assignment of 1 : 1 stoicheiometry for the silver(I) thiocyanate–3Me-py adduct, one formula unit comprising the asymmetric unit of the structure.

The structure, like that of (1), is a two-dimensional network polymer, with layering up one of the crystallographic axes, *a*, with an interpenetrating network of pyridine base moieties.

This structure has an added dimension of complexity in this regard, however, as there are two such layers per unit-cell translation in *a*, related by the glide operation. This aspect of the structure is readily appreciated by reference to Figures 2(*a*) and (*b*), in projection down *c* and *b* respectively, while Figure 2(*c*) shows one of the layers in projection down *a*. From Figure 2(*c*), we see that the structure consists of an intermeshing array of small and large polymer rings. The smaller of the two ring motifs is of the type shown below,



previously observed in the dimeric 1 : 2 silver(I) thiocyanate–triphenylphosphine adduct;[3] in the present case, the sulphur atom has an added bridging function, satisfying one of the co-ordination sites of one of the silver atoms of another nearby dimer, while the fourth co-ordination site of the silver atom is occupied by the pyridine base, reminiscent of the

Table 4. Ligand non-hydrogen geometries for complexes (1)—(3)

		(1)	(2)	(3)
Distances/Å				
	N(1)–C(2)	1.31(2)	1.340(7)	1.34(1)
	N(1)–C(6)	1.33(2)	1.316(8)	1.35(1)
	C(2)–C(3)	1.40(2)	1.378(8)	1.39(2)
	C(3)–C(4)	1.38(2)	1.366(9)	1.38(2)
	C(4)–C(5)	1.34(3)	1.386(10)	1.36(2)
	C(5)–C(6)	1.39(2)	1.374(9)	1.40(1)
	C(2,3)–C(21,31)	1.51(2)	1.493(9)	1.50(2)
	C(6)–C(61)			1.50(2)
Angles/°				
	Ag–N(1)–C(2)	123.9(8)	120.8(4)	119.9(7)
	Ag–N(1)–C(6)	117.1(9)	121.5(4)	119.4(7)
	C(2)–N(1)–C(6)	119.0(12)	117.7(5)	120.3(9)
	N(1)–C(2)–C(3)	121.3(11)	124.1(5)	121.1(10)
	C(2)–C(3)–C(4)	119.4(13)	117.6(5)	119.3(10)
	C(3)–C(4)–C(5)	118.4(13)	118.7(6)	119.4(10)
	C(4)–C(5)–C(6)	119.5(15)	119.8(7)	119.9(10)
	C(5)–C(6)–N(1)	122.2(16)	122.2(6)	120.0(10)
	N(1),C(2)–C(2,3)–C(21,31)	116.8(10)	121.8(5)	117.7(9)
	C(3,4)–C(2,3)–C(21,31)	121.9(11)	120.5(6)	121.2(10)
	N(1)–C(6)–C(61)			119.1(9)
	C(5)–C(6)–C(61)			120.9(10)

Thiocyanate geometries for complexes (1)—(3) (transformations of Table 2 are shown)

		(1)	(2)	(3)
Distances/Å				
	S–C	1.64(1)	1.666(5)	1.66(1)
	C–N	1.17(2)	1.142(7)	1.13(2)
Angles/°				
	S–C–N	179.1(11)	178.8(6)	178.1(11)
	C–N–Ag	168.0(10)	154.9(5)	176.1(9)
	Ag–S–C	105.0(4)	97.9(2)	
	Ag–S$^{\text{i}}$–C$^{\text{i}}$	102.2(4)	103.6(2)	102.9(4)
	Ag–S–Ag	107.3(1)	132.32(7)	

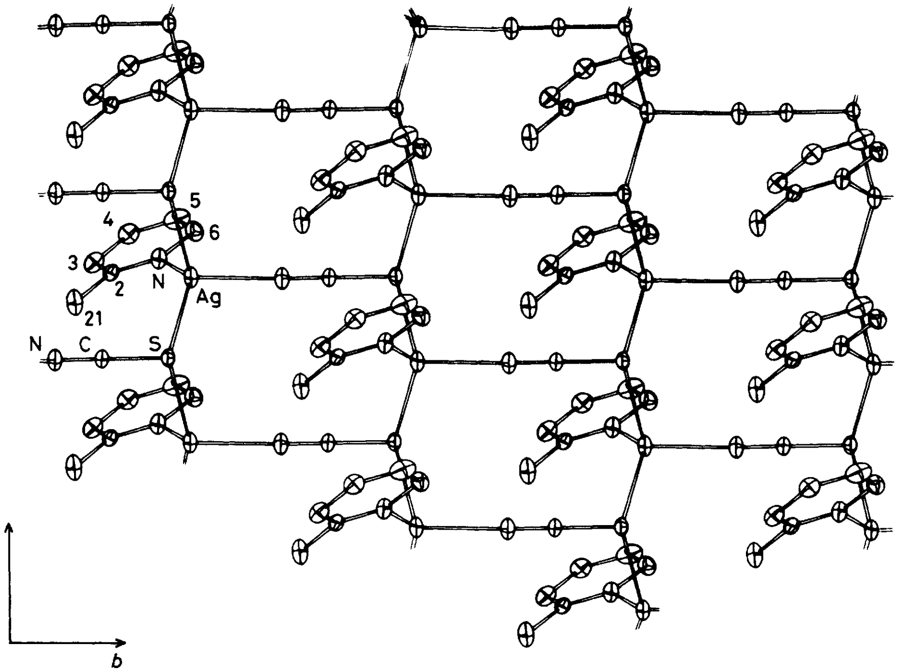


Figure 1. Projection of the structure of (1) down *a* showing the connectivity in the *bc* plane to yield a two-dimensional polymer. 20% Thermal ellipsoids are shown for the non-hydrogen atoms

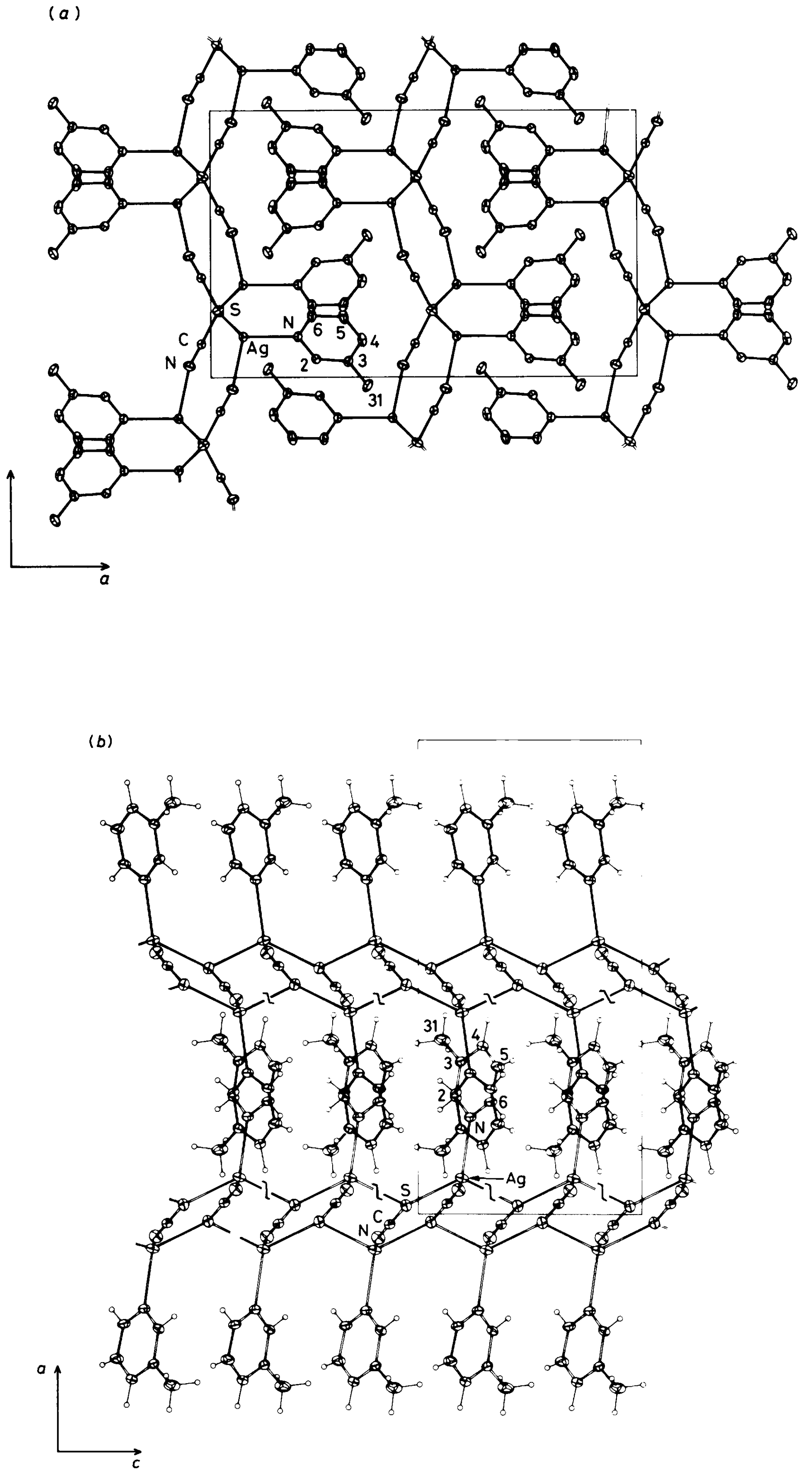


Figure 2. Projection of the structure of (2) down (*a*) the *c* and (*b*) *b* crystallographic axes, showing the layering of the structure and the interpenetration of the pyridine base rings

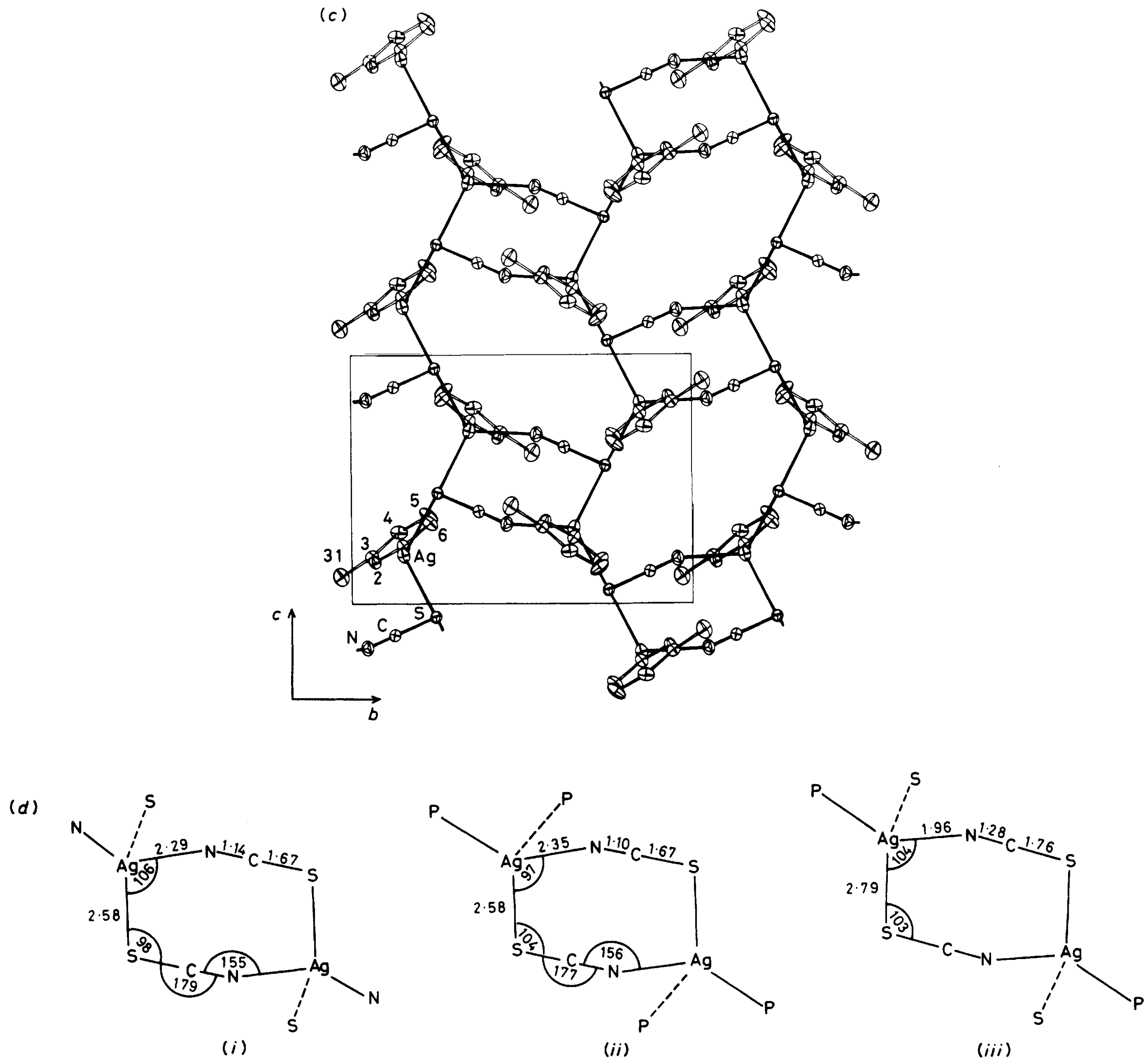


Figure 2 (*continued*) (*c*) Projection of one of the polymer layers of (2) down *a*. (*d*) Comparison of the geometry of (*i*), the dimeric unit of the structure of (2) with that of (*ii*), the 1 : 2 adduct of silver(I) thiocyanate with triphenylphosphine, and (*iii*) with the 1 : 1 adduct of silver(I) thiocyanate with tripropylphosphine

structure of the 1 : 1 silver(I) thiocyanate–tripropylphosphine adduct [4] (a one-dimensional polymer). The geometries of these ring systems are compared in Figure 2(*d*).

As in the structure of (1), the silver atom is pseudo-tetrahedrally four-co-ordinated by a pair of bridging sulphur atoms [Ag–S, 2.578(2) and 2.615(2) Å: S–Ag–S, 108.08(5)°], the pyridine base nitrogen [Ag–N, 2.331(5) Å], and a thiocyanate nitrogen [Ag–N, 2.293(5) Å]. The thiocyanate nitrogen is again pseudo-linearly co-ordinated [C–N–Ag, 154.9(5)°]. The sulphur atom again is 'three-co-ordinate,' but, with an angle sum of 333.6°, is less sharply pyramidal in nature than in (1) where the corresponding sum is 314.5°; in the present structure this is largely a consequence of an enlarged Ag–S–Ag angle [132.32(7), *cf.* 107.3(1)° in (1)].

[{Ag(SCN)(2,6Me$_2$-py)}$_n$] (3).—The structure determination confirms the assignment of 1 : 1 stoicheiometry for the silver(I) thiocyanate–2,6Me$_2$-py adduct, again with one formula unit comprising the asymmetric unit. In this complex, the formula units are linked, with one-dimensional polymeric chains related by the 2_1 screw axis parallel to *b*. A projection of such a chain is given in Figure 3(*a*). It comprises *three-co-ordinate* silver atoms, with the co-ordination sites satisfied by thiocyanate sulphur and nitrogen atoms [Ag–S, 2.474(3) and Ag–N, 2.28(1) Å] and pyridine base nitrogen atoms [Ag–N, 2.275(8) Å]. The angle sum about the silver atom is close to 360° (being 357.1°); the reduction in co-ordination number is presumably a consequence of the increased steric bulk of the pyridine base ligand. The thiocyanate nitrogen, as usual, is pseudo-linearly co-ordinated [Ag–N–C, 176.1(9)°], while Ag–S–C is, as usual, bent [Ag–S–C, 102.9(4)°]. The dihedral angle between the ligand C_5NC_2 plane (σ 0.01 Å)

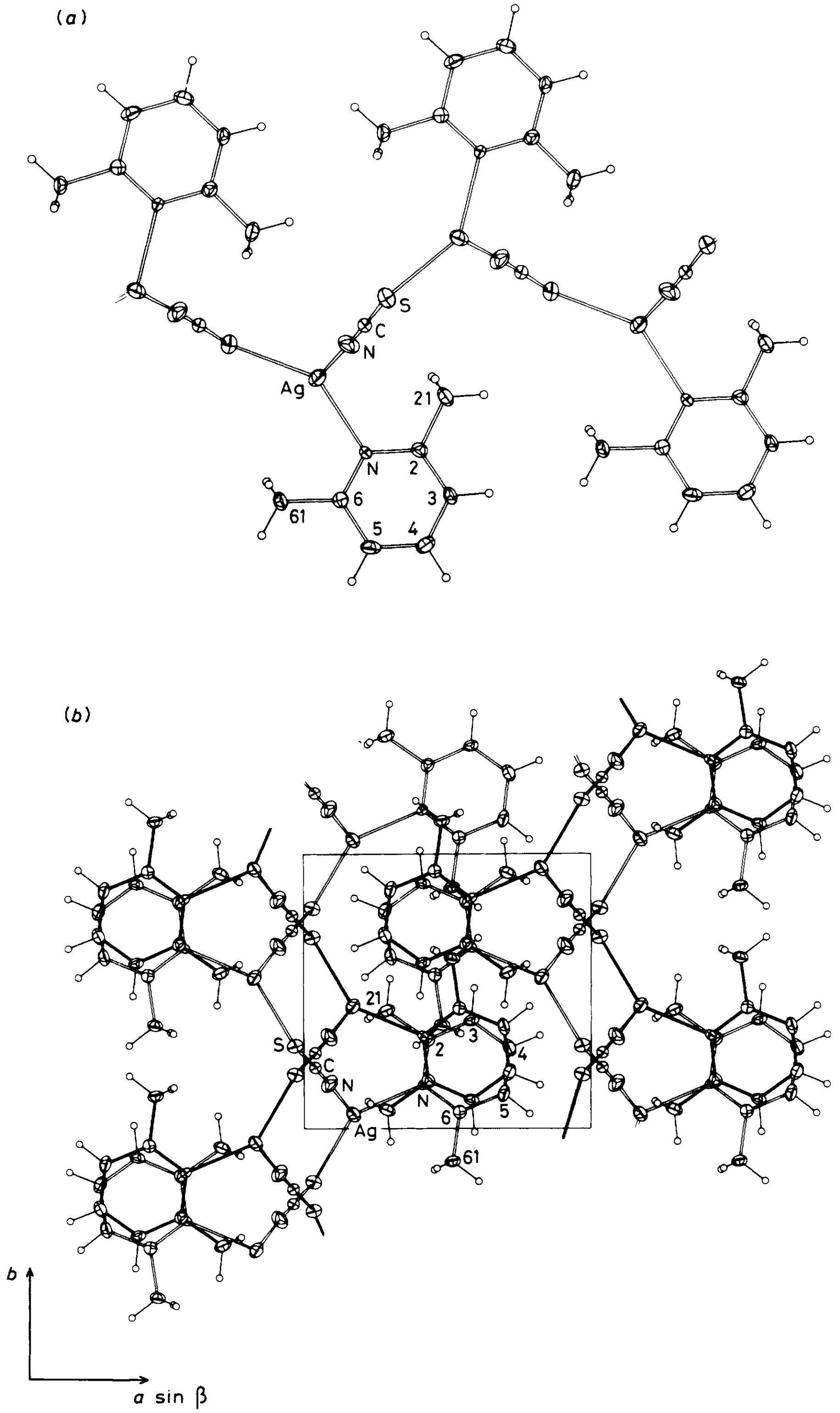


Figure 3. (a) Projection of the structure of (3) down c, showing one strand of the polymer; b is horizontal in the plane of the page. (b) The same, showing the pairwise packing of the polymer strands

and the associated $AgSN_2$ plane (σ 0.113 Å) is 54.6°, with those associated thiocyanate nitrogen and sulphur atoms which do not define the plane deviating by 1.63 and 0.19 Å, respectively. The crystal packing is of interest [Figure 3(b)]. Each strand of the polymer packs in association with its inversion-related pair, so that the pyridine base ring planes lie pseudo-parallel and quasi-normal to c.

[{Ag(SCN)(quin)$_2$}$_n$] (4).—The structure determination establishes a 1 : 2 stoicheiometry for the silver(I) thiocyanate–quinoline adduct. The unit-cell contents comprise four such

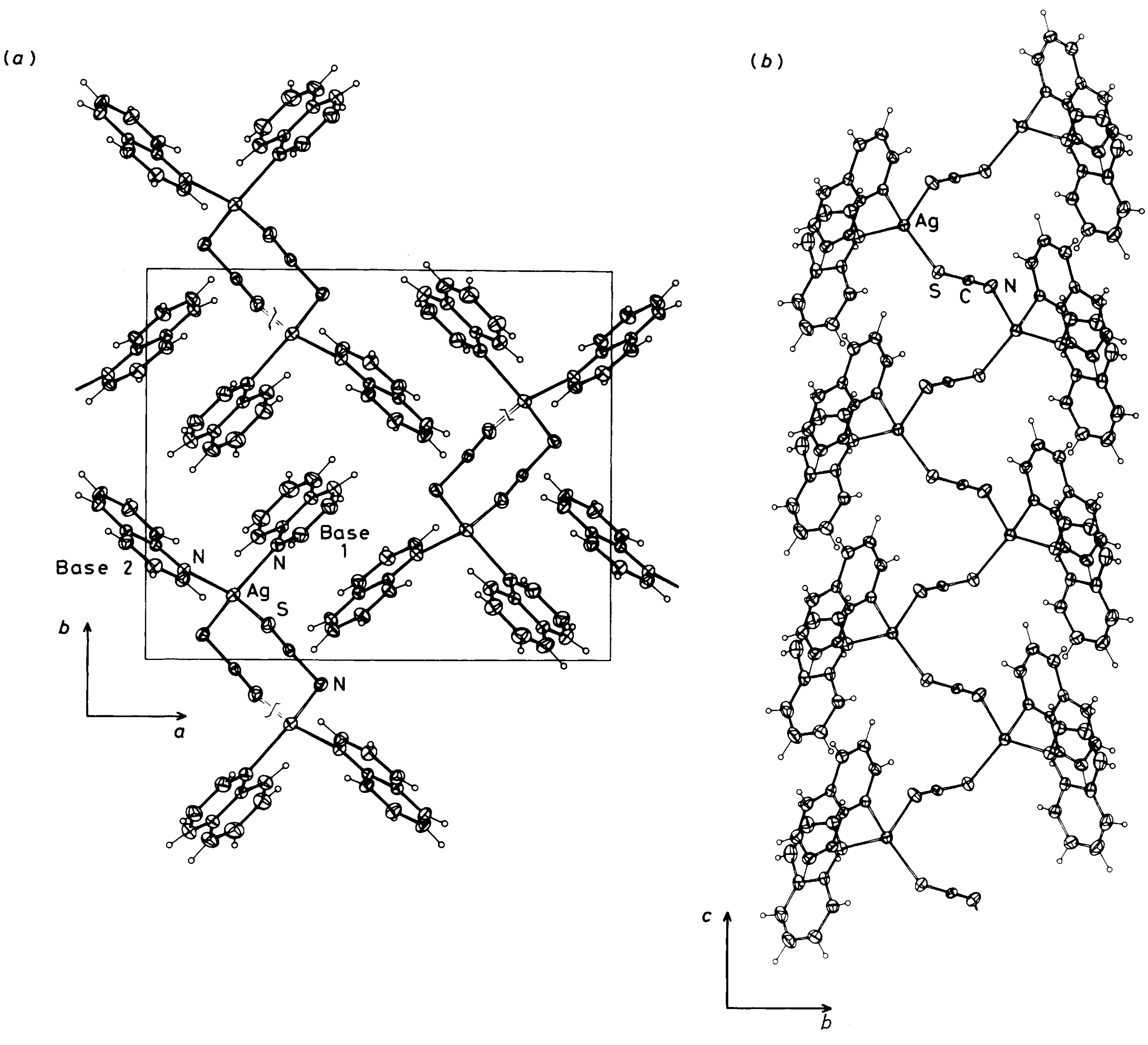


Figure 4. (*a*) Unit-cell contents of (4) projected down *c*; 20% thermal ellipsoids are given for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å. (*b*) A single strand of the polymer projected down *a*

formula units; these, like their counterparts in the other nitrogen base adducts of silver(I) thiocyanate that we have studied are not discrete molecules but infinite polymers. The 1 : 1 Ag(SCN)–base adducts comprise two-dimensional polymers with the thiocyanate co-ordinating three metal atoms, two through the sulphur and one through the nitrogen, in the case of 2- and 3-methylpyridine; however, with the more sterically hindered 2,6-dimethylpyridine we find the thiocyanate co-ordinates two silver atoms only through sulphur and nitrogen, the silver co-ordination number being reduced from four to three, and the resulting polymer being one-dimensional.

A similar situation is found in the present complex. Here, two of the four co-ordination sites of the silver atom are occupied by the quinoline ligands; the remaining two are occupied by the sulphur and nitrogen atoms of a pair of symmetry related thiocyanate groups, so that again an infinite one-dimensional polymer is formed, generated in this case by the two-fold screw axis parallel to *c*. In spite of the change in co-ordination number, the characteristics of the –(SCN)–Ag–(SCN)– polymer string are rather similar in both cases. The repeat distance of the unit-cell length is superimposed by a two-fold screw axis in each case; for [{Ag(SCN)(2,6Me$_2$-py)}$_n$] (3), this is $b = 8.102(2)$ Å, while for the present complex it is $c = 8.009(2)$ Å. The distances Ag–N are 2.28(1) and 2.332(5) Å and Ag–S, 2.474(3) and 2.495(1), respectively, with N–Ag–S, 116.8(3), 119.6(1)°. The silver–pyridine ligand distance is shorter in the 2,6Me$_2$-py adduct as might be expected from the lower co-ordination number [2.275(8) for (3); 2.364(3) and 2.361(4) Å for (4)]. In the present complex Ag–N(CS) is shorter than the Ag–N(quin) distances as might be expected from its π-bonding characteristics; this is not so in the 2,6Me$_2$-py complex where the ligand- and thiocyanate-

Table 5. Ligand geometries for complex (4)

	Ligand 1	Ligand 2
(*a*) Distances/Å		
Thiocyanate ligand		
S–C	1.646(4)	
C–N	1.141(6)	
Quinoline ligands		
N(1)–C(2)	1.320(6)	1.309(7)
C(2)–C(3)	1.389(7)	1.404(8)
C(3)–C(4)	1.356(8)	1.319(11)
C(4)–C(4A)	1.405(7)	1.422(10)
C(4A)–C(8A)	1.414(6)	1.416(6)
C(4A)–C(5)	1.426(6)	1.410(10)
C(5)–C(6)	1.346(8)	1.340(11)
C(6)–C(7)	1.414(8)	1.403(10)
C(7)–C(8)	1.358(7)	1.370(8)
C(8)–C(8A)	1.406(6)	1.401(7)
C(8A)–N(1)	1.367(5)	1.368(6)

(*b*) Angles/°		
Thiocyanate ligand		
Ag–S–C	104.4(1)	
S–C–N	176.8(5)	
C–N–Ag$^{\text{i}}$	142.9(4)	
Quinoline ligands		
Ag–N(1)–C(2)	120.0(3)	115.9(4)
Ag–N(1)–C(8A)	122.2(3)	126.2(3)
C(2)–N(1)–C(8A)	117.8(4)	117.8(4)
N(1)–C(2)–C(3)	123.9(4)	124.1(6)
C(2)–C(3)–C(4)	119.4(5)	119.0(6)
C(3)–C(4)–C(4A)	119.2(5)	120.4(5)
C(4)–C(4A)–C(5)	123.5(4)	124.4(5)
C(4)–C(4A)–C(8A)	118.2(4)	117.0(5)
C(5)–C(4A)–C(8A)	118.3(4)	118.5(5)
C(4A)–C(5)–C(6)	121.5(4)	121.4(6)
C(5)–C(6)–C(7)	119.6(5)	120.5(7)
C(6)–C(7)–C(8)	120.7(5)	120.0(6)
C(7)–C(8)–C(8A)	120.8(4)	120.7(5)
C(8)–C(8A)–N(1)	119.4(4)	119.5(4)
C(8)–C(8A)–C(4A)	119.1(4)	118.9(5)
N(1)–C(8A)–C(4A)	121.5(4)	121.6(4)

Transformation of the asymmetric unit: i $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$.

N–Ag distances are comparable. However, in the present complex, the Ag–N–C angle deviates markedly from the more usual approach to linearity, being 142.9(4)°. Inspection of the structure suggests that this may be a consequence of an unusually close approach to the nitrogen atom by one of the ligand hydrogen atoms [H(12) $\cdots$ N, 2.75 Å], so that the distortion is essentially a consequence of steric crowding.

In the present complex the silver environment is close to *m* in symmetry, with the thiocyanate ligand S,N atoms together with the silver lying in the plane and the quinoline nitrogens to either side. The unit-cell projection (Figure 4) suggests a relationship between this structure and the cyclic $Ag_2(SCN)_2$ building blocks of other structures discussed above.

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