

# The Structure of the Tetrakis(pyridine)silver(I) and Bis-(tributylstibine)silver(I) Complexes in Pyridine Solution

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The structures of the tetrakis(pyridine)silver(I) and bis(tributylstibine)silver(I) complexes in pyridine solution have been investigated by the large angle X-ray scattering technique. The silver(I) ion is tetrahedrally solvated by four pyridines at Ag–N distances of 2.30(2) Å. The pyridine solvated bis(tributylstibine)silver(I) complex has a tetrahedral configuration; the Ag–Sb bond distance is 2.69(2) Å and the Sb–Ag–Sb angle is 110°. The two remaining positions of the tetrahedron are occupied by loosely coordinated pyridine molecules at Ag–N distances of 2.38(2) Å.

The present structural investigation of the tetrakis(pyridine)silver(I) and bis(tributylstibine)silver(I) complexes in pyridine solution is a part of a research programme dealing with complex formation between silver(I) and ligands donating through group VB atoms.<sup>1,2</sup> The soft silver(I) ion is strongly solvated in pyridine, as illustrated by the heats of solvation of Ag<sup>+</sup> in pyridine and in water, viz. –596 and –488 kJ mol<sup>–1</sup>, respectively.<sup>3</sup> The crystal structure of tetrakis(pyridine)silver(I) perchlorate, precipitated from a solution of silver (I) perchlorate in pyridine, has been reported previously.<sup>4</sup> Silver(I) is tetrahedrally coordinated by four pyridine molecules in discrete ions. The perchlorate salt has a solubility of more than 1 M in pyridine, which is sufficient for large angle X-ray scattering (LAXS) studies.

The tetrakis(pyridine)copper(I) and -silver(I) perchlorates are isostructural,<sup>4</sup> and the pyridine solvates of copper(I) and gold(I) are most probably tetrahedral in pyridine solution.<sup>5,6</sup> On the other hand, the solid gold(I) pyridine solvate shows two-coordination around gold.<sup>7</sup> Mononuclear metal-ion solvates always have the maximum coordination number in solution and the silver(I) pyridine solvate is therefore expected to be

tetrahedral in pyridine solution, with a Ag–N bond distance similar to that in the solid, viz. 2.32 Å.<sup>4</sup>

Silver(I) forms fairly strong complexes with a variety of XR<sub>3</sub> ligands (X=P, As or Sb; R=alkyl or phenyl) in pyridine<sup>1,2</sup>. Thermodynamic studies on the complex formation between silver(I) and tri-*n*-butylstibine indicate that both the mono- and bis(ligand) complexes are formed in substitution reactions.<sup>2</sup> A number of structures of silver(I) phosphine complexes have been reported,<sup>8,9</sup> while no silver(I) stibine complex structures have been published. The covalent radius of antimony is about 0.26 Å larger than that of phosphorus<sup>10</sup> and the Ag–Sb bond distance is therefore expected to be about 2.7 Å in the pyridine solvated Ag[Sb(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub><sup>+</sup> complex if silver(I) is tetrahedrally coordinated.

## Experimental

*Preparation of solutions.* The tetrakis(pyridine)silver(I) complex was obtained by dissolving silver(I) perchlorate to saturation in pyridine (solution Agpy<sub>4</sub>). The bis(tributylstibine)silver(I) complex was obtained by dissolving silver(I) perchlorate in a mixture of tri-*n*-butylstibine and

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Table 1. Concentrations (M) in the pyridine solutions studied by large angle X-ray scattering. The linear absorption coefficient,  $\mu(\text{cm}^{-1})$  is calculated for  $\text{MoK}\alpha$  radiation.

Solution	Ag(I)	Sb(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	ClO <sub>4</sub> <sup>-</sup>	C <sub>5</sub> H <sub>5</sub> N	$\mu$
Agpy4	1.12	—	1.12	11.9	4.27
AgSb2	0.934	1.92	0.934	6.6	9.94

pyridine (solution AgSb2). Data for the solutions studied are given in Table 1.

*X-ray scattering experiments.* The X-ray scattering from the free surface of solutions was measured in a large-angle theta-theta diffractometer. The instrument used for the silver(I) solution has been described by Johansson,<sup>11</sup> and the instrument for the stibine was of Seifert GDS-type. The solutions were enclosed in a cylindrical, thin-walled glass container, in order to avoid evaporation and to prevent oxidation of the stibine. The absorption of the glass container and its angle dependence had previously been determined.<sup>12</sup>  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) was employed. The scattered intensities were determined at discrete points in the interval  $4 < \theta < 63$ . An extrapolation of the intensity data for  $\theta < 4$  was necessary, owing to the concave curvature of the meniscus in the glass container. A counting error of 0.35% was achieved by measuring 40 000 counts twice at each sampling point. The fraction of incoherent scattering contributing to the deter-

mined intensity was estimated in the usual manner.<sup>11</sup>

*Data treatment.* The data reduction procedure and corrections applied were as described previously.<sup>13</sup> The experimental intensities were normalized to a stoichiometric unit of volume containing one silver atom. The scattering factors, corrections for anomalous dispersion and values for incoherent scattering were those employed previously.<sup>13</sup> For the silver(I) perchlorate solution, correction was also made for multiple scattering. The reduced intensity curves,  $i_{\text{obs}}(s)$ , multiplied by the scattering parameter,  $s$ , are shown in Figs. 1 and 3. The corresponding electronic radial distribution functions (RDF),  $D(r) - 4\pi r^2 \rho_0$ , were obtained by Fourier transformation (Figs. 2 and 4). The same modification as described previously was used.<sup>11</sup> Spurious peaks below  $1.8 \text{ \AA}$ , which could not be related to interatomic distances within the pyridine molecule or the perchlorate ion, were eliminated by a Fourier procedure.<sup>10</sup>

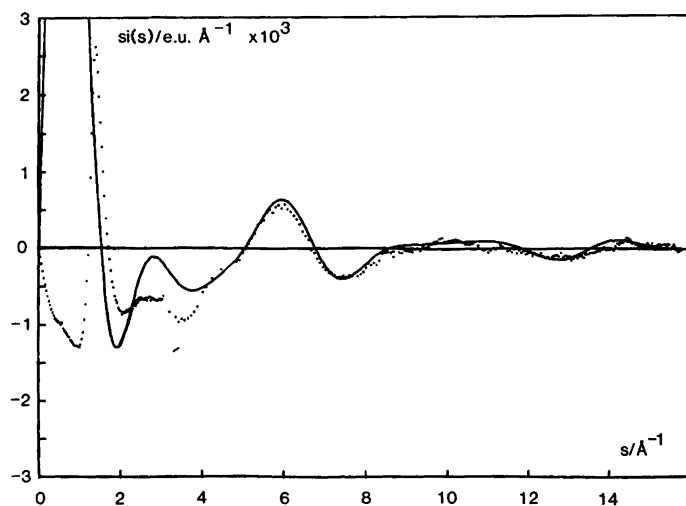


Fig. 1. Experimental (dots) and calculated (solid line)  $si(s)$  values for silver(I) perchlorate in pyridine solution. Parameters given in Table 2 for the  $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4^+$  complex and taken from the literature (Refs. 26 and 28) for the  $\text{ClO}_4^-$  ion and pyridine were used for the theoretical curve.

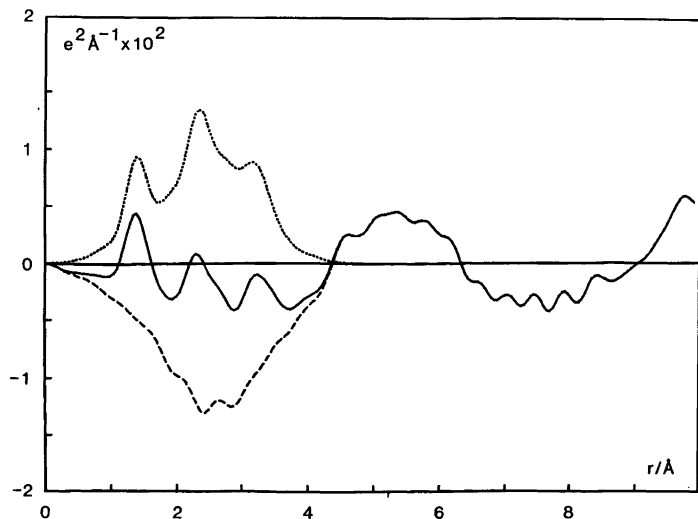


Fig. 2. The function  $D(r) - 4\pi r^2 \rho_0$  and the calculated peak shape for the silver(I) perchlorate pyridine solution, with the same parameters as in Fig. 1. Solid line: experimental curve; dotted line: model function; dashed line: difference plot.

Fig. 3. Experimental (dots) and calculated (solid line)  $si(s)$  values for the bis(tributylstibine)silver(I) complex in pyridine solution. Parameters given in Table 2 for the  $\text{Ag}[\text{Sb}(\text{C}_4\text{H}_9)_3]_2(\text{C}_5\text{H}_5\text{N})_2^+$  complex and taken from the literature (Refs. 26 and 28) for the  $\text{ClO}_4^-$  ion and pyridine were used for the theoretical curve.

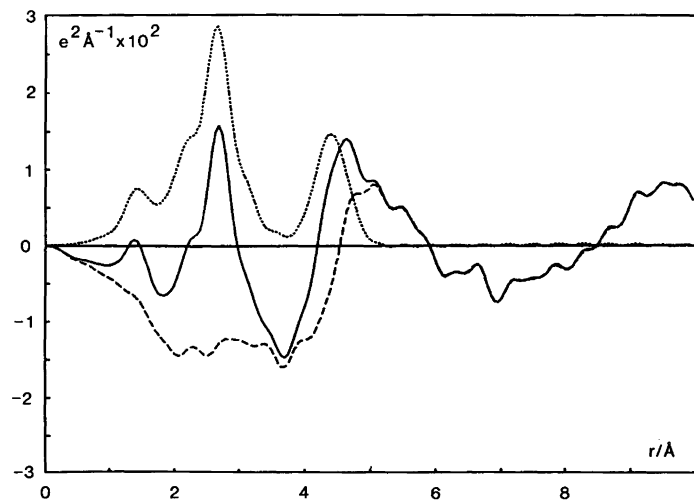
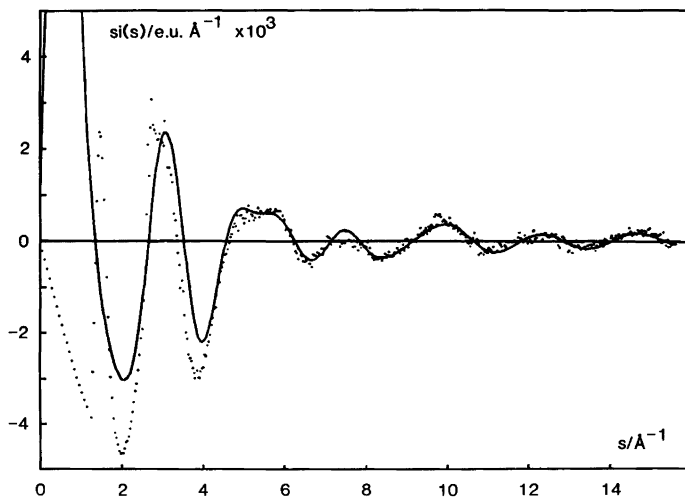


Fig. 4. The function  $D(r) - 4\pi r^2 \rho_0$  and the calculated peak shape for the bis(tributylstibine)silver(I) perchlorate pyridine solution with the same parameters as in Fig. 3. Solid line: experimental curve; dotted line: model function; dashed line: difference plot.

All calculations were carried out using the computer programs KURVLR<sup>14</sup> and STEPLR.<sup>15</sup>

## Results

For the silver(I) solution, peaks corresponding to the Ag–N and Ag–C(1,5) distances in the  $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4^+$  complex are seen at 2.3 and 3.2 Å, respectively, in the RDF (Fig. 2). These distances, and their corresponding temperature coefficients, were refined in the range  $4.0 < s < 16.0 \text{ \AA}^{-1}$ , while the frequency of distances was held fixed. Fixed values were also introduced for the interatomic distances within the pyridine molecule and the perchlorate ion. The parameters for the proposed model of the  $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4^+$  complex are given in Table 2.

The RDF for the bis(tributylstibine)silver(I) complex shows two distinct peaks at 2.7 and 4.4 Å, corresponding to the Ag–Sb and Sb–Sb distances (Fig. 4). The sizes of these peaks indicate two Ag–Sb distances and one Sb–Sb distance, respectively. The shoulder at 2.4 Å in the RDF was assigned to a Ag–N(pyridine) distance. Least-squares refinements of the Ag–Sb and Sb–Sb distances, their temperature coefficients and the Ag–N distance together were performed in the range  $4.4 < s < 15.5 \text{ \AA}^{-1}$ , while the temperature coefficient of the Ag–N distance and all frequencies of distances were refined separately. Fixed parameters were introduced for the pyridine molecule, the perchlorate ion and the hydrocarbon chains. The refinements showed that silver is tetrahedrally coordinated by two stibine ligands and two pyridines. The Sb–Ag–Sb angle is found to be  $110^\circ$ , which shows that the coordination figure is a regular tetrahedron. The parameters for the proposed model of the  $\text{Ag}[\text{Sb}(\text{C}_4\text{H}_9)_3]_2(\text{C}_5\text{H}_5\text{N})_2^+$  complex are given in Table 2.

## Discussion

The structure of the tetrakis(pyridine)silver(I) ion in the solid state and in pyridine solution is found to be identical within the limits of error. The Ag–N distance is substantially longer than the corresponding M–N distances in the tetrakis(pyridine)copper(I) and -gold(I) complexes.<sup>5,6</sup> This order of bond distances is found for all coinage metal complexes, becoming more pronounced with increasing softness of the ligand

**Table 2.** Least-squares refinement of the reduced intensities for the tetrakis(pyridine)silver(I) and bis(tributylstibine)silver(I) complexes in pyridine solution. The refined parameters:  $d$  = distance (Å),  $b$  = temperature coefficient (Å<sup>2</sup>) and  $n$  = number of distances per silver atom are obtained from the reduced intensity curves for the Agpy4 and AgSb2 solutions, respectively. The parameters with estimated errors given in parentheses were refined, while the other parameters were introduced as fixed parameters.

Interaction	Parameter	Solution	
		Agpy4	AgSb2
Ag–N	$d$	2.30(2)	2.38(2)
	$b$	0.0075	0.015(2)
	$n$	4.0	2.3
Ag–C	$d$	3.20(3)	
	$b$	0.016(4)	
	$n$	8.0	
Ag–Sb	$d$		2.680(3)
	$b$		0.0026(4)
	$n$		1.7(1)
Sb–Sb	$d$		4.396(12)
	$b$		0.023(2)
	$n$		0.9(1)
Sb–N	$d$		4.135
	$b$		0.020
	$n$		4.0
Sb–C	$d$		2.15
	$b$		0.005
	$n$		3.0
N–N	$d$	3.74	3.888
	$b$	0.010	0.020
	$n$	6.0	1.0

(Table 3). For acetonitrile (AN), regarded as a borderline donor, the difference in bond distance between silver(I) and gold(I) is 0.06 Å, while this difference is 0.14 Å for pyridine and 0.20 Å for triphenylphosphine; all these complexes are tetrahedral. Gold(I) has a smaller ionic radius than silver(I), due to the  $f$ -shell contribution and to relativistic effects which are especially pronounced for the univalent coinage metal ions. The increasing difference between silver(I) and gold(I) with increasing softness of the ligand is due to the fact that gold(I) is more polarizable than silver(I).

Table 3. Bond distances (Å) in some copper(I), silver(I) and gold(I) complexes.

	M-N in M(py) <sub>4</sub> <sup>+</sup>	M-N in M(AN) <sub>4</sub> <sup>+</sup>	M-P in M(PPh <sub>3</sub> ) <sub>4</sub> <sup>+</sup>	M-Cl in MCl <sub>2</sub>	M-H in MH(g)
Cu(I)	2.05 <sup>a</sup>	1.99 <sup>a</sup>		2.107 <sup>f</sup>	1.463 <sup>i</sup>
Ag(I)	2.30	2.25 <sup>c</sup>	2.68 <sup>d</sup>	2.36 <sup>g</sup>	1.617 <sup>i</sup>
Au(I)	2.16 <sup>b</sup>	2.19 <sup>b</sup>	2.48 <sup>e</sup>	2.257 <sup>h</sup>	1.524 <sup>i</sup>

<sup>a</sup>Ref. 5. <sup>b</sup>Ref. 6. <sup>c</sup>Ref. 16. <sup>d</sup>Ref. 17. <sup>e</sup>Ref. 18, an average value. <sup>f</sup>Ref. 19. <sup>g</sup>Ref. 20. <sup>h</sup>Ref. 21. <sup>i</sup>Ref. 22.

The bis(tributylstibine)silver(I) complex is tetrahedral in pyridine solution. The long Ag-Sb distance and the relatively small C-Sb-C angle (97°) in tributylstibine<sup>23,24</sup> result in there being no steric hindrance between the stibine ligands in the complex ion. The Ag-N(pyridine) distance of 2.38 Å is markedly longer than that in the tetrakis(pyridine)silver(I) complex (see above and Table 2), showing that the pyridines in the Ag[Sb(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub><sup>+</sup> complex are markedly more weakly coordinated than in the latter. A similar Ag-N distance, 2.367 Å, is found in a silver(I) phosphine complex in which silver is coordinated by one phosphorus and three pyridine nitrogens.<sup>25</sup>

It is interesting to note that the coordination around silver(I) remains regular tetrahedral, in spite of the differences in bond strength of the coordinated ligands. The structures of HgX<sub>2</sub>L<sub>2</sub> (X=Cl, Br or I; L=Lewis base) complexes have been extensively studied.<sup>26,27</sup> For mercury(II) halides, the X-Hg-X angle is inversely proportional to the bond strength of Hg-L, and this angle can adopt any value between 90 and 180°. This behaviour has not been seen for silver(I) complexes, which normally have coordination geometries close to tetrahedral, trigonal or linear.

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