Silver(I) Solvation in Some N-Donor Solvents from Ag *K*-edge EXAFS

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It is revealed from the analysis of Ag *K*-edge EXAFS that silver(I) is surrounded tetrahedrally by four solvent molecules in liquid ammonia, pyridine, and acetonitrile solutions with Ag–N distances of 2.31, 2.29, and 2.24 Å, respectively.

The structure of solvated silver(I) in liquid ammonia is an open question. From Raman spectroscopic measurements of liquid ammonia solutions of silver(I) nitrate, Gans and Gill[1] proposed four ammonia molecules bound to silver(I), while Lundeen *et al.*[2] suggested that the solvated silver(I) complex had a distorted octahedral structure with two short and four long Ag–N bonds. In connection with the liquid ammonia system, silver(I) solvation in liquid pyridine and acetonitrile, ligands with different donicity, is also of interest. In the present communication, EXAFS spectroscopy has been applied to determine the solvation structure of silver(I) in these N-donor solvents.

Silver(I) nitrate and perchlorate were thoroughly dried before use and the solvents were dried in the usual way. A liquid ammonia solution was prepared by condensing anhydrous ammonia onto a weighed amount of silver(I) nitrate contained in a cold finger. Pyridine and acetonitrile solutions were prepared by dissolving a weighed amount of silver(I) perchlorate into the dried solvents at room temperature. The silver concentrations were 0.2 mol dm^{-3} for all sample solutions. Ag *K*-edge EXAFS spectra of the ammonia solution were measured using a cryostat containing a mixture of ethanol and dry ice, while those of the other solutions were measured at room temperature. Crystalline diamminesilver(I) nitrate and its aqueous solution were also measured as structure references.

Figure 1 shows the Fourier transforms of $k^3\chi(k)$ obtained over the *k*-region of 3—12 Å^{-1}. The first peak is assignable to
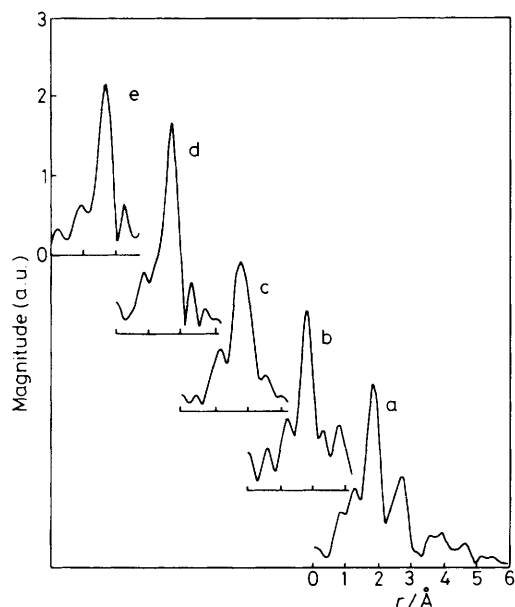
Ag–N bonds in solvated Ag^I complexes. In acetonitrile and pyridine solutions, additional peaks appear corresponding to the interactions between silver(I) and other atoms surrounded by co-ordinating solvent molecules. Structure parameters were extracted from least-squares fittings applied to Fourier filtered modulations of the first peak. The *k*-region used in the fits was 4—11 Å^{-1}. The values of the phase shifts and the backscattering amplitudes were taken from the Teo and Lee table.[3] The final results are given in Table 1. Errors in the distance and the co-ordination number of the first shell were estimated to be ±0.02 Å and ±0.5, respectively. The values of silver(I) hydration are also included for comparison.[4—6]

In liquid ammonia silver(I) is co-ordinated by four ammonia molecules with an Ag–N distance of 2.31 Å. The Tobias model[2] (two short and four long Ag–N bonds) could not reproduce the experimental data satisfactorily. In pyridine solution the solvation number of silver(I) is also four and the Ag–N bond length is close to that in the solid state.[7] In acetonitrile, a poor donating solvent, the Ag–N distance is 2.24 Å, significantly shorter than those found in the other solvents. In the crystal of [Ag(MeCN)$_4$]ClO$_4$, the Ag–N distances are in the range of 2.18—2.33 Å.[8] In the solution, however, the root mean square deviation (σ) of the Ag–N distance is similar to those found for the other solvents, thus indicating a regular tetrahedral co-ordination of acetonitrile molecules to silver(I). The Ag–N distance in acetonitrile solvent, which agrees with the average value (2.26 Å) in the crystal, is regarded as the one within a discrete [Ag(MeCN)$_4$]$^+$ solvate. The Ag–N distance in the solvents may depend on the electronic state of N atoms in co-ordinated solvent molecules. The short Ag–N bond length in acetonitrile solvates may result from the strengthening Ag–N bonds owing to the reverse electron transfer from silver(I) to the π-orbital of the cyanide groups of acetonitrile molecules.

In conclusion, the present EXAFS study has revealed that silver(I) is surrounded by four solvent molecules in ammonia,

Figure 1. Fourier transforms of Ag *K*-edge EXAFS spectra: a, AgClO$_4$–pyridine; b, AgClO$_4$–MeCN; c, AgNO$_3$–NH$_3$(liquid); d, [Ag(NH$_3$)$_2$]$^+$ in H$_2$O; e, [Ag(NH$_3$)$_2$]NO$_3$ solid.

Table 1. Structure parameters of solvated Ag^I in N-donor solvents; *r*, *N*, σ and *DN* represent the distance, the co-ordination number, the root mean square deviation of *r*, and the Gutman donor number, respectively. The values in parentheses are *X*-ray or neutron diffraction data.

	r/Å	*N*	σ/Å	*DN*
NH$_3$	2.31 —	3.7	0.100	59
C$_5$H$_5$N	2.29 (2.32[a])	3.9	0.091	33
MeCN	2.24 (2.26[b])	3.7	0.089	14
H$_2$O	2.37[c] (2.40[d,e])	3.9	—	18
Structure standard				
[Ag(NH$_3$)$_2$]$^+$ in H$_2$O	2.14 (2.24[f])	2[h]	0.062	
[Ag(NH$_3$)$_2$]NO$_3$ solid	2.12 (2.12[g])	2[h]	0.046	

[a] Ref. 7. [b] Ref. 8. [c] Ref. 6. [d] Ref. 4. [e] Ref. 5. [f] Ref. 9. [g] Ref. 10. [h] Fixed.

pyridine, and acetonitrile, as well as in water. It should be noted that in aqueous solution, diamminesilver(I) assumes a stable linear co-ordination without further water molecules in the co-ordination sphere at distances less than 3.0 Å.[9,10] Recently, Bjerrum reported the presence of triammine-silver(I) in highly ammoniacal aqueous solution.[11] The tetra-amminesilver(I) complex is formed under extreme conditions such as in liquid ammonia.

The X-ray absorption spectra were measured using the EXAFS facilities installed at the Beam Line 10B in the Photon Factory at the National Laboratory for High-Energy Physics (KEK-PF).

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