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# Coordination Chemistry of the Solvated Silver(I) Ion in the Oxygen Donor Solvents Water, Dimethyl Sulfoxide, and *N*,*N*′-Dimethylpropyleneurea

**Ingmar Persson* and Kersti B. Nilsson**

*Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015,*
*SE-750 07 Uppsala, Sweden*

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The hydrated and dimethyl sulfoxide and *N*,*N*′-dimethylpropyleneurea solvated silver(I) ions have been characterized structurally in solution by means of extended X-ray absorption fine structure (EXAFS) and large-angle X-ray scattering (LAXS). The coordination chemistry of the hydrated and dimethyl sulfoxide solvated silver(I) ions has been reevaluated because of different results from the EXAFS and LAXS methods reported previously. Consistent results are obtained with a linearly distorted tetrahedral model with two short and approximately two long Ag–O bond distances: mean Ag–O bond lengths of 2.32(1) and 2.54(1) Å for the hydrate, 2.31(1) and 2.48(2) Å for the dimethyl sulfoxide solvate, and 2.31(1) and 2.54(2) Å for the *N*,*N*′-dimethylpropyleneurea solvate, in solution.

## Introduction

The coordination chemistry of the hydrated silver(I) ions in solution has been studied by many groups. Unfortunately, contradictory results are reported depending on the method used. The hydration of the silver(I) ion is very weak, and it crystallizes without coordinated water molecules in most salts; only one compound with an isolated hydrated silver(I) ion, $[Ag(OH_2)_2]^+$, has been characterized by crystallography.[1] It is agreed that the hydrated silver(I) ion binds four water molecules in a tetrahedral configuration in an aqueous solution.[2,3] However, there is a general trend in the reported mean Ag−O bond distances in the hydrated silver(I) ion depending on the method used: large-angle X-ray scattering (LAXS) and large-angle neutron scattering (LANS), on the one hand, and extended X-ray absorption fine structure (EXAFS), on the other hand.[2,3] From LAXS studies, the mean Ag−O bond distance is reported to be 2.38−2.45 Å in concentrated (3.0−4.3 mol·dm$^{-3}$) aqueous solutions of silver(I) perchlorate or nitrate,[4,5] and similar results, 2.43−2.45 Å, are reported in extremely concentrated aqueous solutions/melts of silver(I) perchlorate (9 mol·dm$^{-3}$)[4] and silver(I) nitrate (14.2 mol·dm$^{-3}$),[4,5] respectively, where the silver(I) ion is mainly surrounded by anions. A neutron scattering study on an aqueous solution of silver(I) perchlorate reported a Ag−O bond distance of 2.42 Å.[6] The Ag−O bond distances obtained on the same systems by EXAFS are significantly shorter, 2.31−2.36 Å.[7−9] The LAXS and EXAFS techniques are complementary. The LAXS method is sensitive for long and weak interactions but with a lower resolution due to a smaller momentum range, normally 0−16 Å$^{-1}$. On the other hand, the EXAFS method has a larger momentum range, normally 4−28 Å$^{-1}$, and thereby a higher resolution of short well-defined distances, but has only weak sensitivity for long distances with broad distance distribution.[10,11] New LAXS and EXAFS data have been collected on the hydrated silver(I) ion in this study to secure that previously reported results are correct. By using the same

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* To whom correspondence should be addressed. E-mail: ingmar.persson@kemi.slu.se.

(1) Makhmudova, N. K.; Sharipov, K. T.; Khodashova, T. S.; Porai-Koshits, M. A.; Parpiev, N. A. *Dokl. Akad. Nauk SSSR* **1985**, *280*, 1360.
(2) Johansson, G. *Adv. Inorg. Chem.* **1992**, *31*, 159 and references cited therein.
(3) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1187 and references cited therein.
(4) Maeda, M.; Maegawa, Y.; Yamaguchi, T.; Wakita, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2545.
(5) Yamaguchi, T.; Johansson, G.; Holmberg, B.; Maeda, M.; Ohtaki, H. *Acta Chem. Scand., Ser. A* **1984**, *38*, 437.
(6) Sandström, M.; Neilson, G. W.; Johansson, G.; Yamaguchi, T. *J. Phys. C: Solid State Phys.* **1985**, *18*, L1115.
(7) Yamaguchi, T.; Lindqvist, O.; Boyce, J. B.; Claesson, T. *Acta Chem. Scand., Ser. A* **1984**, *38*, 423.
(8) Seward, T. M.; Henderson, C. M. B; Charnock, J. M.; Dobson, B. R. *Geochim. Cosmochim. Acta* **1996**, *60*, 2273.
(9) Moreno-Diaz, S. Doctoral Thesis, University of Seville, Seville, Spain, 1998.
(10) Persson, I.; Sandström, M.; Yokoyama, H.; Chaudhry, M. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 21.
(11) Hagfeldt, C.; Kessler, V. K.; Persson, I. *Dalton Trans.* **2004**, 2142.

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type of model of the hydrated silver(I) ion as before, a regular tetrahedral configuration around the silver(I) ion, the previously reported results were confirmed (see the Results and Discussion section).

A molecular dynamics simulation based on ab initio quantum mechanical forces with molecular dynamics proposes that the silver(I) ion has an irregular-shaped first hydration shell with a mean coordination number of about 5.5 in an aqueous solution (0.1096 mol·dm$^{-3}$).[13] The calculated Ag—O bond distances, ca. 2.6 Å, are, however, significantly longer than those experimentally obtained in this and previous studies.[12] An animation from this theoretical study shows the preferred linear distortion (http://www.molvision.com). In a Monte Carlo simulation of an aqueous silver(I) solution (0.1976 mol·dm$^{-3}$), a mean coordination number of about 6 and a Ag—O bond distance of 2.3 Å are reported.[13] In both studies, a poorly defined second hydration sphere at 4.5—4.7 Å is reported. Theoretical studies of the hydrated silver(I) ion in silver(I)—water clusters in a gaseous phase show a very fine balance between two-, three-, and four-coordinated species, with the lowest energy for a planar three-coordinated complex and two linear two-coordinated ones where additionally one or two other water molecules are hydrogen bonded to the water molecules bound to silver.[14]

The reported results from experimental LAXS/LANS and EXAFS have proposed that the hydrated silver(I) has a tetrahedral configuration, but the mean Ag—O bond distance differs depending on the method used, while simulation studies propose a coordination number close to 6. This strongly indicates that the present model of the hydrated silver(I) ion based on experimental studies, a regular tetrahedron, is not fully correct, and new models have to be tested in order to find a model fitting both LAXS and EXAFS data and maybe give an input for further refined simulations.

The structure of the dimethyl sulfoxide solvated silver(I) ion in solution has been reported from a LAXS study to be regularly tetrahedral with a mean Ag—O bond distance of 2.42 Å.[15] The solvation of the silver(I) ion is stronger in dimethyl sulfoxide than in water.[16] Despite this fact, the only reported silver(I) compound with coordinated dimethyl sulfoxide molecules, $AgClO_4 \cdot 2(CH_3)SO$, contains infinite chains with doubly bridged dimethyl sulfoxide-*O* molecules. In addition, two perchlorate oxygen atoms bind weakly to silver(I), completing a distorted six-coordination around silver with a mean Ag—O bond distance of 2.48 Å.[17] The coordination of perchlorate oxygen atoms to silver(I) makes this compound very explosive.[17] EXAFS data and new LAXS data have been recorded on the dimethyl sulfoxide solvated silver(I) ion in solution in this study.

*N*,*N*′-Dimethylpropyleneurea or 3,4,5,6-tetrahydro-2*H*-pyrrolidone (DMPU) has two methyl groups close to the oxygen atom that coordinates to the metal ions. This causes it to be very space demanding at coordination to a metal ion and the coordination number to be often lower in DMPU solvates than most other oxygen donor solvates; e.g., the nickel and zinc ions are five- and four-coordinated in DMPU, respectively, while they are six-coordinated in octahedral fashion in water and dimethyl sulfoxide.[18,19]

**Table 1.** Concentrations (mol dm$^{-3}$) of the Aqueous Dimethyl Sulfoxideand DMPU Solutions Used in the EXAFS and LAXS Measurements

| sample | [M$^+$] | [X$^-$] | [solvent] | $\rho$/(g cm$^{-3}$) | $\mu$/cm$^{-1}$ |
|---|---|---|---|---|---|
| $AgClO_4$ in water | 2.040 | 2.140 | 47.366 | 1.3000 | 7.77 |
| $AgCF_3SO_3$ in $Me_2SO$ | 1.015 | 1.015 | 13.904 | 1.2678 | 11.50 |
| $AgCF_3SO_3$ in DMPU | 0.515 | 0.515 | 8.825 | 1.0654 | 4.17 |

## Experimental Section

**Solvents.** All water used was Millipore Q filtered. Dimethyl sulfoxide (Merck) and DMPU (BASF) were distilled under reduced pressure over calcium hydride (Fluka) and stored in dark bottles over 3-Å molecular sieves.

**Chemicals and Preparation of Solutions.** Weighed amounts of anhydrous silver perchlorate, $AgClO_4$ (G. F. Smith), were dissolved in water, and anhydrous silver trifluoromethanesulfonate, $AgCF_3SO_3$, in dimethyl sulfoxide and DMPU.

The concentrations of the studied solutions are summarized in Table 1.

**EXAFS: Data Collection.** Silver K-edge X-ray absorption spectra were recorded at the wiggler beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). The EXAFS station was equipped with a Si[220] double-crystal monochromator. SSRL did operate at 3.0 GeV and a maximum current of 100 mA. The data collections were performed in transmission mode. Higher order harmonics were reduced by detuning the second monochromator to 70% of the maximum intensity at the end of the scans. The energy scales of the X-ray absorption spectra were calibrated by assigning the first inflection point of the K edge of a silver foil to 25 514 eV.[20] For each sample, 3—6 scans were averaged, giving satisfactory data ($k^2$-weighted) in the $k$ range 2—15.5 Å$^{-1}$.

**EXAFS: Data Analysis.** The *EXAFSPAK*[21] and *GNXAS*[22,23] program packages were used for the data treatment. The *GNXAS* code is based on the calculation of the EXAFS signal and a subsequent refinement of the structural parameters.[22,23] The *GNXAS* method accounts for multiple-scattering (MS) paths, with correct treatment of the configurational average of all of the MS signals to allow fitting of correlated distances and bond distance variances (Debye—Waller factors). A correct description of the first coordination sphere of the studied complex has to account for asymmetry in the distribution of the ion—solvent distances.[24,25] Therefore, the Ag—O two-body signals associated with the first coordination shells were modeled with Γ-like distribution functions, which depend on

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(12) Armunato, R.; Schwenk, C. F.; Rode, B. M. *J. Phys. Chem. A* **2003**, *107*, 3132.

(13) Dubois, V.; Archirel, P.; Boutin, A. *J. Phys. Chem. B* **2001**, *105*, 9363.

(14) Fox, B. S.; Beyer, M. K.; Bondybey, V. E. *J. Am. Chem. Soc.* **2002**, *124*, 13613.

(15) Gaizer, F.; Johansson, G. *Acta Chem. Scand., Ser. A* **1988**, *42*, 259.

(16) Wei, L.; Persson, I. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2223.

(17) Cassel, A.; Björk, N.-O. *Acta Chem. Scand., Ser. A* **1976**, *30*, 235.

(18) Bobicz, D.; Kristiansson, O.; Persson, I. *J. Chem. Soc., Dalton Trans.* **2002**, 4201.

(19) Lundberg, D.; Eriksson, L.; Persson, I. *J. Mol. Liq.* **2006**, in press.

(20) Thompson, A.; Attwood, D.; Gullikson, E.; Howells, M.; Kim, K.-J.; Kirz, J.; Kortright, J.; Lindau, I.; Pianatta, P.; Robinson, A.; Scofield, J.; Underwood, J.; Vaughan, D.; Williams, G.; Winick, H. *X-ray Data Booklet*, LBNL/PUB-490 revision 2; Lawrence Berkeley National Laboratory: Berkeley, CA, 2001.

(21) George, G. N.; Pickering, I. J. *EXAFSPAK—A Suite of Computer Programs for Analysis of X-ray Absorption Spectra*; SSRL: Stanford, CA, 1993.

(22) Filipponi, A.; Di Cicco, A.; Natoli, C. R. *Phys. Rev. B* **1995**, *52*, 15122.

(23) Filipponi, A.; Di Cicco, A. *Phys. Rev. B* **1995**, *52*, 15135.

**Table 2.** Mean Bond Distances, $d$/Å, Number of Distances, $N$, Temperature Coefficients, $b^2$/Å$^2$, Half-Heights at Half-Width, $l$/Å ($l = \sqrt{2b} = 2\sigma$), and Third Cumulant Factor Describing the Asymmetry, $C_3$/Å$^3$, of the Hydrated and Dimethyl Sulfoxide Solvated Silver(I) Ions in Solution As Determined by LAXS and EXAFS at Room Temperature

| | interaction | $N$ | $d$ | $b^2/\sigma^2$ | $l$ | $C_3$ |
|---|---|---|---|---|---|---|
| | Aqueous Solution of Silver Perchlorate, LAXS Determination | | | | | |
| $Ag(OH_2)_4^+$ | Ag−O | 4 | 2.423(5) | 0.0133(6) | 0.163(4) | |
| | $Ag\cdots O_{II}$ | 8 | 4.76(5) | 0.084(8) | 0.41(2) | |
| $Ag(OH_2)_4^+$ | Ag−O | 2 | 2.320(2) | 0.0086(2) | 0.131(2) | |
| | Ag−O | 2 | 2.480(2) | 0.0122(2) | 0.156(2) | |
| | $Ag\cdots O_{II}$ | 8 | 4.763(6) | 0.0745(10) | 0.306(5) | |
| $ClO_4^-$ | Cl−O | 4 | 1.453(2) | 0.0031(2) | 0.078(2) | |
| | $Cl-(O)\cdots O_w$ | 8 | 3.04(4) | 0.024(2) | 0.22(8) | |
| water bulk | $O_w\cdots O_w$ | 2 | 2.890(12) | 0.020(6) | 0.20(3) | |
| | Aqueous Solution of Silver Perchlorate, EXAFS Determination | | | | | |
| $Ag(OH_2)_4^+$ | Ag−O | 4 | 2.367(3) | 0.0083(4) | 0.182(3) | $<1 \times 10^{-6}$ |
| $Ag(OH_2)_4^+$ | Ag−O | 2 | 2.319(2) | 0.0037(4) | 0.122(7) | $<1 \times 10^{-6}$ |
| | Ag−O | 2 | 2.477(5) | 0.0073(7) | 0.171(8) | $<1 \times 10^{-6}$ |
| | Dimethyl Sulfoxide Solution of Silver Trifluoromethanesulfonate, LAXS Determination | | | | | |
| $Ag(OS(CH_3)_2)_4^+$ | Ag−O | 4 | 2.429(4) | 0.0091(5) | 0.125(7) | |
| | Ag- - -S | 4 | 3.465(3) | 0.0218(5) | 0.117(5) | |
| $Ag(OS(CH_3)_2)_4^+$ | Ag−O | 2 | 2.320(4) | 0.0031(5) | 0.125(7) | |
| | Ag−O | 2 | 2.52(1) | 0.0071(8) | 0.148(9) | |
| | Ag- - -S | 2 | 3.358(3) | 0.0084(5) | 0.117(5) | |
| | Ag- - -S | 2 | 3.578(6) | 0.019(1) | 0.122(5) | |
| $ClO_4^-$(DMSO) | Cl−O | 4 | 1.425(2) | 0.0020(2) | 0.063(3) | |
| | Dimethyl Sulfoxide Solution of Silver Trifluoromethanesulfonate, EXAFS Determination | | | | | |
| $Ag(OS(CH_3)_2)_4^+$ | Ag−O | 4 | 2.323(4) | 0.0163(4) | 0.255(3) | $<1 \times 10^{-6}$ |
| | Ag- - -S | 4 | 3.393(8) | 0.0372(8) | 0.386(5) | |
| | S- - -O | 4 | 1.515(4) | 0.0075(5) | 0.173(6) | |
| | $\angle Ag-O_1-S_1$ | 4 | 122.8(0.9) | | | |
| $Ag(OS(CH_3)_2)_4^+$ | $Ag-O_1$ | 2 | 2.310(2) | 0.0078(3) | 0.177(3) | $<1 \times 10^{-6}$ |
| | $Ag-O_2$ | 2 | 2.54(1) | 0.037(1) | 0.38(1) | $3.7 \times 10^{-3}$ |
| | | | $R_m(Ag-O_2) = 2.48(1)$ | | | |
| | Ag- - -$S_1$ | 2 | 3.452(6) | 0.0176(7) | 0.265(5) | |
| | Ag- - -$S_2$ | 2 | 3.717(12) | 0.0264(12) | 0.325(8) | |
| | S1- - -$O_1$ | 2 | 1.525(3) | 0.0043(3) | 0.131(5) | |
| | S2- - -$O_2$ | 2 | 1.532(4) | 0.0075(5) | 0.173(6) | |
| | $\angle Ag-O_1-S_1$ | 2 | 127.3(1.0) | | | |
| | $\angle Ag-O_2-S_2$ | 2 | 132.4(1.9) | | | |
| | DMPU Solution of Silver Trifluoromethanesulfonate, LAXS Determination | | | | | |
| $Ag(DMPU)_4^+$ | Ag−O | 4 | 2.416(4) | 0.0106(5) | 0.223(4) | |
| | Ag- -C | 4 | 3.367(4) | 0.0120(9) | 0.349(5) | |
| $Ag(DMPU)_4^+$ | $Ag-O_1$ | 2 | 2.313(2) | 0.0036(3) | 0.158(3) | |
| | $Ag-O_2$ | 2 | 2.537(5) | 0.0076(2) | 0.36(1) | |
| | Ag- - -$C_1$ | 2 | 3.310(8) | 0.0063(11) | 0.29(1) | |
| | Ag- - -$C_2$ | 2 | 3.450(12) | 0.012(2) | 0.55(2) | |
| | DMPU Solution of Silver Trifluoromethanesulfonate, EXAFS Determination | | | | | |
| $Ag(DMPU)_4^+$ | Ag−O | 4 | 2.321(4) | 0.0124(4) | 0.223(4) | $2.3 \times 10^{-4}$ |
| | | | $R_m(Ag-O) = 2.301(4)$ | | | |
| | Ag- - -C | 4 | 3.381(10) | 0.0305(9) | 0.349(5) | |
| | C- - -O | 4 | 1.260(5) | 0.0080(6) | 0.179(6) | |
| | $\angle Ag-O-C$ | 4 | 139.7(1.9) | | | |
| $Ag(DMPU)_4^+$ | $Ag-O_1$ | 2 | 2.308(2) | 0.0062(3) | 0.158(3) | $<1 \times 10^{-6}$ |
| | $Ag-O_2$ | 2 | 2.537(5) | 0.033(2) | 0.36(1) | $1.3 \times 10^{-3}$ |
| | | | $R_m(Ag-O_2) = 2.49(1)$ | | | |
| | Ag- - -$C_1$ | 2 | 3.38(1) | 0.021(1) | 0.29(1) | |
| | Ag- - -$C_2$ | 2 | 3.54(3) | 0.076(5) | 0.55(2) | |
| | C1- - -$O_1$ | 2 | 1.265(5) | 0.0041(5) | 0.128(8) | |
| | C2- - -$O_2$ | 2 | 1.30(5) | 0.0072(10) | 0.17(1) | |
| | $\angle Ag-O_1-C_1$ | 2 | 140.3(1.6) | | | |
| | $\angle Ag-O_2-C_2$ | 2 | 132.2(6.0) | | | |

[a] In the presence of significant asymmetry, the position of the peak maximum, $R_m$/Å, has been calculated.

four parameters, namely, the coordination number $N$, the average distance $R$, the mean-square variation $\sigma$, and the skewness $\beta$. The $\beta$ term is related to the third cumulant $C_3$ through the relation $C_3 = \sigma^3\beta$, and $R$ is the first moment of the function $4\pi\int g(r)^2\,dr$. It is important to stress that $R$ is the average distance and not the position of the maximum of the distribution ($R_m$).

The standard deviations given for the refined parameters in Table 2 are obtained from $k^2$-weighted least-squares refinements of the EXAFS function $\chi(k)$ and do not include systematic errors of the measurements. These statistical error estimates provide a measure of the precision of the results and allow reasonable comparisons, e.g., of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the $E_0$ value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the

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(24) Filipponi, A. *J. Phys.: Condens. Matter* **1994**, *6*, 8415.

(25) Hedin, L.; Lundqvist, B. I. *J. Phys. C: Solid State Phys.* **1971**, *4*, 2064.

separate complexes is within ±0.01−0.02 Å for well-defined interactions. The "standard deviations" given in the text have been increased accordingly to include estimated additional effects of systematic errors.

**LAXS.** The scattering of the Mo Kα X-ray radiation ($\lambda = 0.7107$ Å) from the free surfaces of aqueous and dimethyl sulfoxide solutions of silver perchlorate was measured by means of a large-angle Θ−Θ diffractometer. The solutions were contained in a Teflon cup inside an airtight radiation shield with beryllium windows. The scattered radiation was monochromatized in a focusing LiF crystal monochromator, and the intensity was measured at discrete points in the range $1 < \Theta < 65°$; the scattering angle was 2Θ. The number of counts accumulated was 100 000 at each preset angle, and the entire angular range was scanned twice, which corresponds to a statistical error of about 0.3%. The divergence of the primary X-ray beam was limited by 1°, $^1/_4$°, or $^1/_{12}$° slits for different Θ regions, with overlapping data for scaling purposes. The experimental setup and the theory of the data treatment and modeling have been presented elsewhere.[26] All data treatment was carried out by means of the KURVLR program.[27] The experimental intensities were normalized to a stoichiometric unit of volume containing one silver atom, using the scattering factors $f$ for neutral atoms, including corrections for anomalous dispersion,[28] $\Delta f'$ and $\Delta f''$, and values for Compton scattering.[29] Least-squares refinements of the model parameters were carried out by means of the STEPLR program,[30] where the expression $U = \sum[si_{\text{exp}}(s) - si_{\text{calc}}(s)]^2$ is minimized. The refinement of the model parameters was made for data in the high-$s$ region, where the intensity contribution from the long-range distances can be neglected.[31] To obtain a better alignment of the intensity function before the refinements, a Fourier back-transformation procedure was used to correct the $i_{\text{exp}}(s)$ functions by removing spurious nonphysical peaks below 1.2 Å in the experimental radial distribution function (RDF).[32]

## Results and Discussion

**Hydrated Silver(I) Ion in an Aqueous Solution.** The previously proposed regular tetrahedral model of the hydrated silver(I) ion in an aqueous solution has assumed equidistant Ag−O bonds (see the Introduction). By application of such a model to the newly collected LAXS and EXAFS data, the refined structure parameters were in complete agreement with those reported previously for the hydrated silver(I) ion (see Table 2). However, by application of a model with two different Ag−O bond distances, equal or better fits of the experimental LAXS and EXAFS data were obtained, *and* the results from the two methods are in agreement (see Table 2). Two Ag−O bonds are much shorter and stronger, 2.32(1) Å, than the other approximately two, 2.48(2) Å, most probably in a linearly distorted configuration (Table 2 and Figures 1a and 2a and S1a and S2 in the Supporting Information); neither of these distances shows any significant asymmetry. The number of distances has been fixed in the refinements because this parameter is strongly correlated with the temperature factor coefficient, $b$, and refinement of both parameters simultaneously is in most cases meaningless. Especially, the number of water molecules at a long distance is uncertain, and a mean number larger than 2, as proposed by theoretical studies, is possible. The structure parameters obtained for the hydrated silver(I) ions are summarized in Table 2. The fits, using the parameters obtained from a regular tetrahedral model from the LAXS data, applied on the EXAFS data, and the parameters obtained from the corresponding fit from the EAXFS data, applied on the LAXS data, are given in Figures S3 and S4 in the Supporting Information for comparison with Figures 1a and 2.

The number of weakly bound water molecules is uncertain, and it is possible that more than two water molecules are present. It is not possible from the present experiments to estimate any angles in the hydrate complex because no MS in the inner coordination sphere is observed in the EXAFS spectrum due to weak Ag−O bonds in low symmetry. No O- - -O distances could be observed in the RDF of the LAXS study for the same reason. Two simulation studies propose mean coordination numbers of the hydrated silver(I) ion in an aqueous solution of 5.5 and 6, respectively,[12,13] but the reported Ag−O bond distances are longer, 2.6 Å, and slightly shorter, 2.3 Å, respectively, than the experimentally obtained ones in this and previous studies; the expected Ag−O bond distance in regular six-coordination is 2.49 Å.[33,34] A second hydration sphere is characterized with an $\text{Ag}\cdots\text{O}_{\text{II}}$ distance of 4.76(2) Å with a very broad distance distribution in both models, seen as a very large temperature factor coefficient (Table 2); the contributions from $\text{Ag}\cdots\text{O}_{\text{II}}$ distances from $\text{Ag-O}_{\text{sh}}$ and $\text{Ag-O}_{\text{lo}}$ are expected to be different but cannot be separated. There are approximately two water molecules bound to each coordinated water molecule in the first hydration sphere. The very broad distance distribution in the second hydration sphere is most probably caused by the large bond distance distribution in the inner coordination sphere. The peak at ca. 4 Å in the difference function from the LAXS measurements of the aqueous solution of silver(I) perchlorate is also found in other aqueous solutions with large low-valent metal ions[35−38] or large cluster anions.[39] The origin of this distance is yet uncertain, but it seems that it is O−O distances in water arranged in a nonclassical way. This indicates that the structure of the hydrated silver(I) ion in an aqueous solution depends on the hydrogen-bonding situation around

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(26) Stålhandske, C. M. V.; Persson, I.; Sandström, M.; Kamienska-Piotrowicz, E. *Inorg. Chem.* **1997**, *36*, 3174.

(27) Johansson, G.; Sandström, M. *Chem. Scr.* **1973**, *4*, 195.

(28) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(29) (a) Cromer, D. T. *J. Chem. Phys.* **1969**, *50*, 4857. (b) Cromer, D. T.; Mann, J. B. *J. Chem. Phys.* **1967**, *47*, 1892.

(30) Molund, M.; Persson, I. *Chem. Scr.* **1985**, *25*, 197.

(31) Sandström, M.; Persson, I.; Ahrland, S. *Acta Chem. Scand., Ser. A* **1978**, *32*, 607.

(32) Levy, H. A.; Danford, M. D.; Narten, A. H. *Data Collection and Evaluation with an X-ray Diffractometer, Designed for the Study of Liquid Structure*; Report ORNL-3960; Oak Ridge National Laboratory: Oak Ridge, TN, 1966.

(33) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(34) Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 2105.

(35) Jalilehvand, F.; Spångberg, D.; Lindqvist-Reis, P.; Hermansson, K.; Persson, I.; Sandström, M. *J. Am. Chem. Soc.* **2001**, *123*, 431.

(36) D'Angelo, P.; Persson, I. *Inorg. Chem.* **2004**, *43*, 3543.

(37) Persson, I.; Jalilehvand, F.; Sandström, M. *Inorg. Chem.* **2002**, *41*, 192.

(38) Rosdahl, J.; Persson, I.; Kloo, L.; Ståhl, K. *Inorg. Chim. Acta* **2004**, *357*, 2624.

(39) Lyxell, D.-G.; Pettersson, L.; Persson, I. *Inorg. Chem.* **2001**, *40*, 584.

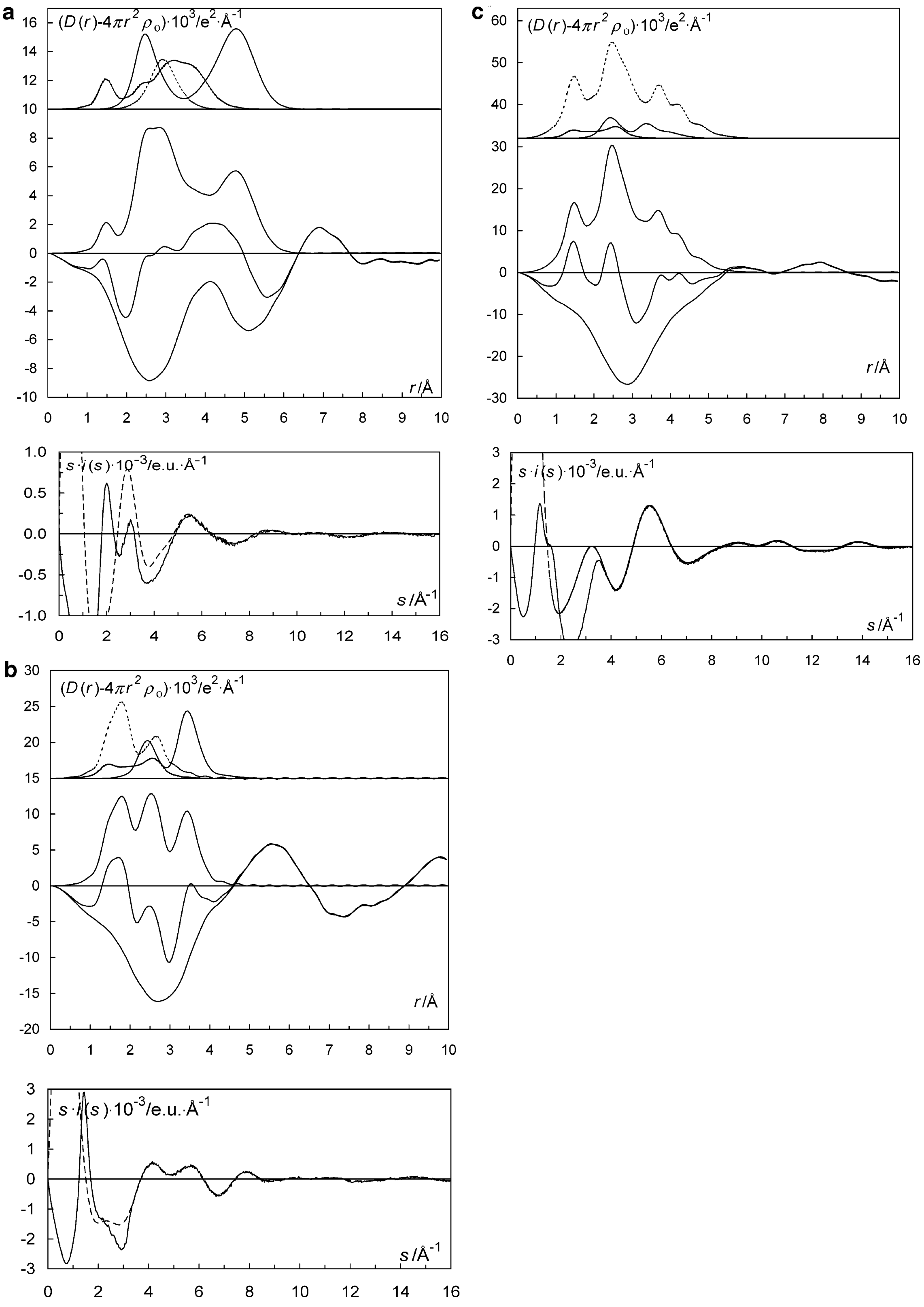

**Figure 1.** LAXS. (Top) (a) Individual peak shapes for all contributing species in the 2.00 mol dm$^{-3}$ aqueous solution of silver perchlorate: Ag−O interactions in the first hydration shell (solid line), the hydrated perchlorate ion (dashed line), and O···O distances in aqueous bulk (dotted line). (Middle) Experimental $D(r)-4\pi r^2\rho_0$ (solid line); model (dashed line); difference (dash−dotted line). (Bottom) Reduced LAXS intensity functions: $si(s)$ (solid line); model $si_{calc}(s)$ (dashed line). (b) Individual peak shapes for all contributing species in the 1.02 mol dm$^{-3}$ dimethyl sulfoxide solution of silver trifluoromethanesulfonate: Ag−O and Ag···S in the first solvation shell (solid line), the trifluoromethanesulfonate ion (dashed line), and distances within the dimethyl sulfoxide molecule (dotted line). (Middle) Experimental $D(r)-4\pi r^2\rho_0$ (solid line); model (dashed line); difference (dash−dotted line). (Bottom) Reduced LAXS intensity functions; $si(s)$ (solid line); model $si_{calc}(s)$ (dashed line). (c) Individual peak shapes for all contributing species in the 0.515 mol dm$^{-3}$ DMPU solution of silver trifluoromethanesulfonate: Ag−O and Ag···C in the first solvation shell (solid line), the trifluoromethanesulfonate ion (dashed line), and distances within the DMPU molecule (dotted line). (Middle) Experimental $D(r)-4\pi r^2\rho_0$ (solid line); model (dashed line); difference (dash−dotted line). (Bottom) Reduced LAXS intensity functions: $si(s)$ (solid line); model $si_{calc}(s)$ (dashed line).

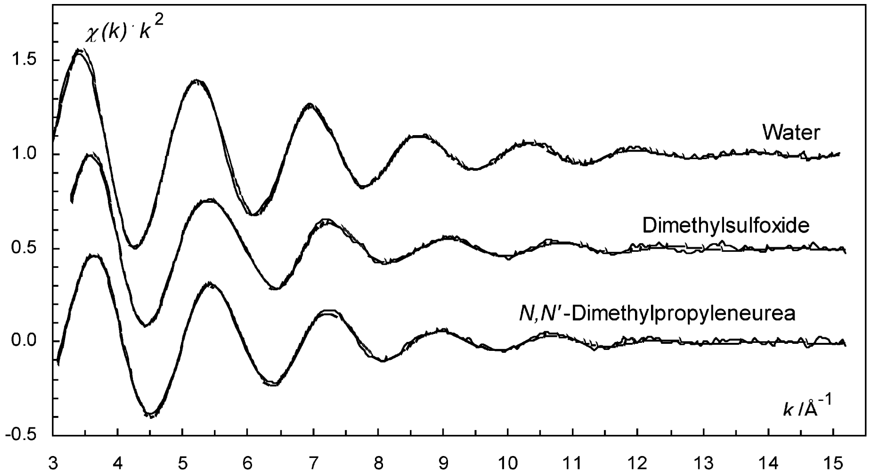

**Figure 2.** $k^2$-weighted EXAFS data of experimental (solid line) and theoretical (dashed line) data of the hydrated and dimethyl sulfoxide and DMPU solvated silver(I) ions in solution.

the hydrated ion. It is, therefore, very important at molecular dynamics simulations of hydrated species that a large number of water molecules are included in the simulations in order to obtain realistic conditions; none of the structures proposed from theoretical studies in the gaseous phase[14] fits the experimental data in an aqueous solution presented in this study, while the simulations with a large excess of water molecules[12,13] are fairly close to the experimental observations.

The proposed linearly distorted structure of the hydrated silver(I) ion can be explained by the vibronic coupling of pseudodegenerate electronic states, a pseudo-Jahn–Teller effect (PJTE). Such a strong mixing will give rise to a lower symmetry. In contrast to the Jahn–Teller effect, the PJTE distortion is especially prominent in systems where a formation of a new covalence in the low-symmetry configuration can take place.[40] The results from molecular dynamics simulations, in comparison to the experimental results in this study, may indicate that the covalent contribution to the shortest and strongest Ag–O bonds in the hydrate has not been emphasized enough.

**Dimethyl Sulfoxide Solvated Silver(I) Ion.** By application of a regular tetrahedral model to the dimethyl sulfoxide solvated silver(I) ion, the newly recorded LAXS data, 2.419(8) Å, are in complete accordance with the result reported previously, 2.42 Å[11] (see the Introduction) while the EXAFS data gave a shorter mean Ag–O bond distance, 2.32 Å (see Table 2). By implementation of a model with two different Ag–O bond distances also in this case, the results from the methods become coherent. As found for the hydrated silver(I) ion, there is a large difference between the short and long Ag–O bond lengths, 2.31(1) and 2.54(2) Å, respectively. The long Ag–O bond distance is significantly asymmetric with a peak maximum at 2.48(2) Å, $C_3 = 3.7 \times 10^{-3}$ Å$^3$. The structure parameters obtained for the dimethyl sulfoxide solvated silver(I) ion are summarized in Table 2, and the fit of LAXS and EXAFS data are given in Figures 1b and 2b and S1b and S2 in the Supporting Information.

**DMPU Solvated Silver(I) Ion.** By application of a regular tetrahedral model to the DMPU solvated silver(I) ion, the LAXS and EXAFS data gave mean Ag–O bond distances of 2.42 and 2.32 Å, respectively (see Table 2). By implementation of a model with two different Ag–O bond distances, the results from the methods become coherent. The difference between the short and long Ag–O bonds, 2.31(1) and 2.54(2) Å, respectively, is the same as that in dimethyl sulfoxide. The long Ag–O bond distance is also in this case significantly asymmetric with a peak maximum at 2.49(2) Å, $C_3 = 1.3 \times 10^{-3}$ Å$^3$. The structure parameters obtained for the DMPU solvated silver(I) ion are summarized in Table 2, and the fit of LAXS and EXAFS data are given in Figures 1c and 2c and S1c and S2 in the Supporting Information.

## Conclusions

The solvated silver(I) ion oxygen donor solvents seem to have a linearly distorted structure with two short and at least two significantly longer Ag–O bonds, 2.31 and 2.48 Å, respectively. If regular models are applied, a significant difference in the results between EXAFS and LAXS data is obtained, while coherent results are obtained with the proposed low-symmetry model. The soft coordination properties of the silver(I) ion are clearly seen in the results presented in this study by two short bonds, which certainly has a significant covalent contribution, while the remaining solvent molecules are most probably bound through weak, mainly electrostatic, interactions. The number of solvent molecules beyond the strongly bound ones is therefore poorly defined.

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(40) Bersuker, I. B. *Electronic structure and properties of transition metal compounds. Introduction to the theory*; John Wiley & Sons, Inc.: New York, 1996.

nology Program, and by the Department of Energy, Office of Biological and Environmental Research.

**Supporting Information Available:** Normalized XANES spectra, Fourier transforms of the studied silver(I) complexes, and LAXS and EXAFS data (Figures S1−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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