An EXAFS Spectroscopic Study of Solvates of Copper(I) and Copper(II) in Acetonitrile, Dimethyl Sulfoxide, Pyridine, and Tetrahydrothiophene Solutions and a Large-Angle X-ray Scattering Study of the Copper(II) Acetonitrile Solvate in Solution

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X-ray absorption edge and EXAFS spectra of the acetonitrile, dimethyl sulfoxide, pyridine and tetrahydrothiophene solvated copper(I) ions and the acetonitrile and dimethyl sulfoxide solvated copper(II) ions have been measured in solution. Analysis reveals that the copper(I) solvates are most probably tetrahedral, and the following Cu–solvate bond distances have been found: Cu–N = 1.99(2) Å in acetonitrile, Cu–O = 2.09(4) Å in dimethyl sulfoxide, Cu–N = 2.06(1) Å in pyridine, and Cu–S = 2.30(1) Å in tetrahydrothiophene. The copper(II) solvates are most probably Jahn–Teller distorted octahedrons, and the following equatorial Cu–solvate bond distances have been found: Cu–N = 1.99(1) Å in acetonitrile, and Cu–O = 1.98(1) Å in dimethyl sulfoxide. An 1.0 M solution of copper(II) trifluoromethanesulfonate in acetonitrile has been studied by means of the large-angle X-ray scattering technique, and the following Cu–N and Cu–C distances have been found for the $Cu(CH_3CN)_4^{2+}$ complex: 1.99(1) and 3.12(1) Å, respectively. No solvate molecules in the axial positions could however be seen by any of the techniques used. The structure of the tetraaquacopper(I) ion has been assumed to be tetrahedral, and from a correlation between the difference in bond length between the copper(I) and copper(II) solvates and the disproportionation constants of copper(I) in the solvent, the Cu–O bond distance is predicted to be approximately 0.14 Å longer than the equatorial Cu–O distances in the Jahn–Teller distorted hexaaquacopper(II) complex, thus about 2.13 Å.

Complex formation between copper(I) and the halides has been studied in dimethyl sulfoxide (Me_2SO), acetonitrile, pyridine, and tetrahydrothiophene (THT).[2–5] In order to interpret and understand the thermodynamics of the complex formation reactions it is important to know the structure of the copper(I) solvates in solution. The free energies, $\Delta G\,^\circ_{sv}$, and the heats, $\Delta H\,^\circ_{sv}$, of solvation of the copper(I) ion have been determined in dimethyl sulfoxide, acetonitrile, pyridine, and tetrahydrothiophene.[6–8] The $-\Delta G\,^\circ_{sv}$ values increase in the order Me_2SO < acetonitrile < pyridine < THT, while the $-\Delta H\,^\circ_{sv}$ values increase in the order Me_2SO < acetonitrile < THT < pyridine. The different order may be explained by the fact that THT most probably has a fairly pronounced bulk structure.[9,10] The bulk structure is partly broken up at the solvation of ions and complexes.[8] This breakup of the solvent structure is much more energy consuming in a solvent with a pronounced bulk structure, such as water or THT, than in solvents with a low degree bulk order, such as pyridine.

The disproportionation constant, K_D, for the reaction $2Cu^+ \leftrightarrow Cu^0 + Cu^{2+}$ differs substantially between different solvents. The disproportionation constants for copper(I) are found to be about 10^6, 2, 10^{-14}, and 10^{-21} M^{-1} in water,[11] dimethyl sulfoxide,[12]

pyridine,[4] and acetonitrile,[3] respectively. K_D is a measure of the difference in free energy of solvation between copper(I) and copper(II). Since the bond distances in the solvates also reflect the free energies of solvation, the differences in copper–solvate distances between the copper(I) and copper(II) solvates will vary between solvents. The enormous variation in the free energies of solvation is therefore expected to give rise to significant variation in the *differences* of bond distances between the copper(I) and copper(II) solvates. Direct determination of the Cu–solvate distances for copper(I) and copper(II) in the different solvents is thus important in order to test the correlation between the structure and thermodynamics of these complexes. Ultimately, an improved understanding of Cu–solvate interactions will be important for interpreting electron-transfer rates and copper ion transport in biological materials.

Experimental Section

Chemicals. [$Cu(CH_3CN)_4$]ClO_4 was prepared as described elsewhere.[13]

[$Cu(C_5H_5N)_6$](ClO_4)$_2$ was prepared by mixing solid [$Cu(H_2O)_6$](ClO_4)$_2$ (G. F. Smith) and pyridine. An immediate color change of the solid from blue to deep violet was observed. The solid [$Cu(C_5H_5N)_4$](ClO_4)$_2$ formed was dried in air and it was treated with pyridine twice more.

[$Cu(C_5H_5N)_4$]ClO_4 was prepared as follows. A slurry of [$Cu(C_5H_5N)_4$](ClO_4)$_2$ in pyridine was degassed with nitrogen for some minutes in an E-flask, and metallic copper was added to the slurry. The temperature of the reaction mixture was slowly increased to about 75 °C under nitrogen atmosphere and heavy stirring. At this temperature copper(II) reacts fairly fast with the metallic copper and forms a yellow solution of copper(I). When all copper(II) had reacted, the pyridine solution was cooled to room temperature. On addition of benzene to this solution pale yellow crystals of [$Cu(C_5H_5N)_4$]ClO_4 precipitated. These were filtered off under a stream of dry nitrogen. The compound was dried under reduced pressure and stored in a desiccator under a nitrogen atmosphere. In course of time

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the compound turns greenish yellow, probably due to oxidation of the ultimate surface layers to copper(II) but without any bulk oxidation. When $[Cu(C_5H_5N)_4]ClO_4$ is oxidized by air, a light blue copper(II) compound is formed.

Anhydrous copper(II) trifluoromethanesulfonate, $Cu(CF_3SO_3)_2$, was prepared by reacting copper(II) carbonate and trifluoromethylsulfonic acid in an aqueous slurry. Water was evaporated off, and the compound was dried in a desiccator at reduced pressure over phosphorus pentoxide at about 100 °C. The anhydrous copper(II) trifluoromethanesulfonate thus obtained is white.

Solvents. *Acetonitrile* (Aldrich) was distilled over phosphorus pentoxide before use. *Dimethyl sulfoxide* (Aldrich) was distilled over calcium hydride (Fluka) under reduced pressure and stored over 3-Å molecular sieves. *Pyridine* (Aldrich, analytical grade) and *tetrahydrothiophene* (Aldrich) were stored over 3-Å molecular sieves without further purification.
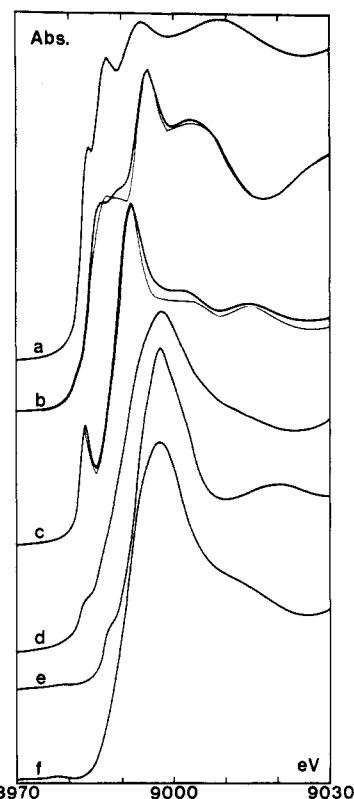
Preparation of Solutions. A 1.21 M copper(I) perchlorate solution in THT was prepared by dissolving $[Cu(CH_3CN)_4]ClO_4$ in THT. Dry nitrogen was bubbled through the solution at about 70 °C in order to remove the acetonitrile, and the evaporated volume was replaced with THT. Small amounts of acetonitrile in the solution will however not disturb the measurements because acetonitrile will not be coordinated to copper(I) in THT due to the much stronger solvating abilities of THT.[7] A 20 mM copper(I) dimethyl sulfoxide solution was prepared by adding metallic copper to a 10 mM copper(II) trifluoromethanesulfonate solution. Dry nitrogen was bubbled through the solution in order to remove traces of dimethyl sulfide, and the solution was heated to about 50 °C to speed up the reproportionation reaction.

Saturated solutions of copper(I) perchlorate in acetonitrile and pyridine were prepared by dissolving $[Cu(CH_3CN)_4]ClO_4$ and $[Cu(C_5H_5N)_4]$-ClO_4, respectively, in the pure solvents.

The copper(II) trifluoromethanesulfonate solutions were prepared by dissolving anhydrous copper(II) trifluoromethanesulfonate in dimethyl sulfoxide and acetonitrile to give 0.5 and 1.0 M solutions, respectively.

EXAFS Measurements. X-ray absorption data were measured at the Stanford Synchrotron Radiation Laboratory, SSRL, using beam lines 1-5 (bending magnet) and 4-2 (wiggler station) under dedicated conditions, 3.0 GeV and 30–80 mA. Monochromatic radiation was obtained using a Si(220) double-crystal monochromator. The monochromator was detuned by 50% for harmonic rejection. All spectra were measured as transmission data with an average of three to six scans collected per sample. The X-ray absorption spectra were converted to an energy scale using copper foil as internal standard with the first inflection point of the copper foil K-edge defined as 8980.3 eV. The EXAFS data were processed by using standard procedures for preedge subtraction, spline fit and removal, and Fourier filtering.[14] The curve fitting analysis of the EXAFS data depends on the assumption that the phase shifts and amplitudes are transferable among compounds of similar chemical structure.[14,15] Data were modeled using a nonlinear least-squares fitting procedure with empirical amplitude and phase parameters taken from EXAFS data for $Cu(acetylacetonate)_2$ (Cu–O), $Cu(imidazole)_4(NO_3)_2$ (Cu–N), and Cu-(diethyldithiocarbamate)$_2$ (Cu–S). For fitting the outer shells in acetonitrile solvates, the Cu–C parameters were taken from the outer shells for solid $Cu(CH_3CN)_4ClO_4$, thus empirically accounting at least in part for the effects of multiple scattering.

X-ray Scattering Experiments. The X-ray scattering from the free surface of a solution was measured in a large-angle θ–θ diffractometer[16] of Seifert GDS type. The copper(II) trifluoromethanesulfonate acetonitrile solution was enclosed in a cylindrical thin-walled glass container, in order to avoid evaporation. The absorption of the glass container and its angle dependence[17] have previously been determined. Mo Kα (λ = 0.7107 Å) radiation was used as an X-ray source. The scattered intensities were determined at discrete points in the interval $4° < \theta < 66°$, separated by 0.0335 in s, where $s = 4\pi\lambda^{-1}(\sin \theta)$ and the scattering angle is 2θ. An explanation of the intensity data at $\theta < 4°$ was necessary due to the upward meniscus in the glass container. A counting error of 0.35% was achieved by measuring 40 000 counts twice at each sampling point. The

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Figure 1. Absorption edge spectra for (a) Cu^+ in tetrahydrothiophene (a), (b) Cu^+ in pyridine (thick line) and $Cu(C_5H_5N)_4ClO_4$ (thin line), (c) Cu^+ in acetonitrile (thick line) and $Cu(CH_3CN)_4ClO_4$ (thin line), (d) Cu^+ in dimethyl sulfoxide, (e) Cu^{2+} in acetonitrile, (f) and Cu^{2+} in dimethyl sulfoxide.

fraction of incoherent scattering contributing to the intensity determinations has been estimated in the usual manner.[18]

Treatment of X-ray Scattering Data. The same data reduction procedure and corrections as described previously were applied.[19] The experimental intensities were normalized to a stoichiometric unit of volume containing one copper atom. The scattering factors, the corrections for anomalous dispersion and the values for incoherent scattering were the same as before.[19] Spurious peaks below 1.5 Å which could not be related to interatomic distances within the acetonitrile molecule or the trifluoromethanesulfonate ion were removed by a Fourier transformation procedure.[16] All calculations were carried out by means of the computer programs KURVLR[20] and STEPLR.[21]

Results

X-ray Absorption Edges. The X-ray absorption edges of the samples studied are shown in Figure 1. As expected,[22] the edges for the copper(I) samples occur at lower energy than those for copper(II). In addition, within a particular oxidation state the edge energies decrease with increasing solvation of the metal ion; for copper(I) Me$_2$SO < acetonitrile < pyridine < THT, and for copper(II) acetonitrile < Me$_2$SO << pyridine. Thus, the edge for solvated copper(I) in dimethyl sulfoxide or acetonitrile is 5 eV higher in energy than that for copper(I) in THT. By comparison, the change in edge energy between copper(II) and copper(I) in a given solvate is only 2 eV. The tetrakis(acetonitrile)-copper(I) and tetrakis(pyridine)copper(I) complexes have identical absorption edges in solid and solution, respectively, indicating that their structures in the solid state and in solution must be very similar.

THT Solution. The Fourier transform of the EXAFS data for the copper(I) perchlorate solution indicates the presence of a

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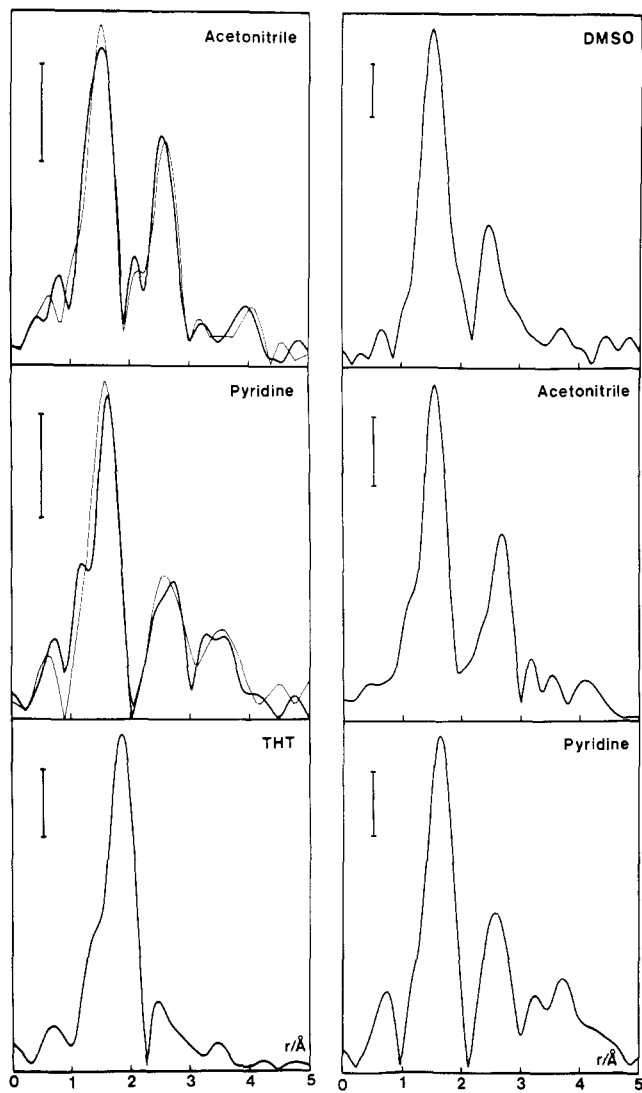
Figure 2. Fourier transforms for EXAFS data, calculated using k^3 weighted data over the range $k = 3-13$ Å^{-1}. Left: Copper(I) in acetonitrile, pyridine, and tetrahydrothiophene (top to bottom). For acetonitrile and pyridine, the light line is solid and the dark line is solution. Right: Copper(II) in dimethyl sulfoxide and acetonitrile solution and Cu(C$_5$H$_5$N)$_4$(ClO$_4$)$_2$(s). For each Fourier transform, the absolute magnitude is indicated by a vertical bar of length 5.0.

single shell of scatterers around copper (the Fourier transforms for all of the EXAFS data are shown in Figure 2, and the corresponding EXAFS spectra are included as supplementary material). The curve-fitting gives a good fit with a single shell of sulfur atoms, indicating four sulfur atoms at approximately 2.30 Å. Since the shape of the copper edges is similar to other edges where copper(I) is tetrahedrally coordinated, copper(I) is most probably solvated by THT in a tetrahedral fashion. The average Cu^I–S bond distance for tetrahedral copper(I) in the solid state is found to be in the range 2.32–2.36 Å.[23-27] The Cu^I–S distance of 2.30 Å for the THT solvate obtained by EXAFS measurements is slightly shorter than previously found, but longer than expected for a three-coordinated Cu^I–S site.[28] No second shell of scatterers is observed. This may be due to either heterogeneity in the Cu–SC$_4$H$_8$ coordination geometry or to

flexibility in the THT ring, both of which could lead to a broad distribution of Cu$\cdots$C distances and thus EXAFS nondetectability. When anhydrous copper(II) trifluoromethanesulfonate is dissolved in THT, copper(II) is spontaneously reduced to copper(I) by the solvent. The structure of the THT solvated copper(II) ion could therefore not be determined.

Pyridine Solutions. The Fourier transforms of the EXAFS data for the tetrakis(pyridine)copper(I) ion show the presence of at least two shells of low-Z scatters around copper(I), both in the solid and in solution. The edges of the solution and the solid are very similar and highly structured, possibly reflecting the importance of the pyridine π-interaction and Cu$\cdots$C multiple scattering. In solid tetrakis(pyridine)copper(I) perchlorate, copper(I) is coordinated by four pyridines in a regular tetrahedral configuration.[29] The EXAFS data indicate that a similar structure is present in pyridine solution. The Cu–N bond distance is slightly longer in solution, 0.01 Å, but this difference is not significant. The relative Debye–Waller factor of the Cu–N bond is almost the same in the solid ($\sigma^2 = 0.0036$ Å^2) and in solution ($\sigma^2 = 0.0043$ Å^2). This indicates that there are no significant differences between the Cu–N bonds in solution and in the solid. A shell of carbons is present at about 3.0 Å, which fits nicely with the expected Cu–N–C angle of 120°. Quantitative analysis of the outer-shell scattering from pyridine requires inclusion of multiple scattering effects; however, these effects are small for the 3.0-Å Cu–C shell.[30] The Cu–C distance is less well-defined in solution than in the solid; i.e., this shell has a larger Debye–Waller factor, which probably reflects the greater mobility of the coordinated pyridines in solution.

Solid Cu(C$_5$H$_5$N)$_4$(ClO$_4$)$_2$. The Fourier transform of the EXAFS data for solid Cu(C$_5$H$_5$N)$_4$(ClO$_4$)$_2$ show at least two shells of low-Z scatters around copper(II). The Cu–N and Cu–C distances refine to 2.01 and 3.0 Å, respectively, which is in close agreement with the Cu–N and Cu–C distances obtained crystallographically.[31]

Acetonitrile Solutions. The Fourier transforms of the EXAFS data for the copper(I) perchlorate solution and the solid tetrakis-(acetonitrile)copper(I) perchlorate both show two principal shells of low-Z scatterers around the copper, with some evidence for a third shell at longer distance. The absorption edges of this complex have identical shapes in solution and in the solid state, and are typical of those seen for tetrahedral copper(I) complexes. The same Cu^I–N bond distance of 1.99 Å is observed for both samples, and this is in agreement with the Cu^I–N bond distance found in solid Cu(CH$_3$CN)$_4$ClO$_4$.[32] The difference in the relative Debye–Waller factor for the Cu–N shell between the solid ($\sigma^2 = 0.0038$ Å^2) and the solution ($\sigma^2 = 0.0040$ Å^2) is insignificant. Interestingly, the two Cu$^I\cdots$C distances are significantly shorter in solution than in the solid state. This suggests that the Cu^I–N–C angle deviates from linearity in solution. The average angle in solution is calculated by triangulation to be approximately 152 ± 10°, although the true angle may be slightly larger since this calculation neglects the difference in multiple scattering for linear vs bent Cu–N–C groups. In contrast, this angle is almost linear, 174 ± 6°, in the solid. This difference suggests that the coordinated acetonitrile molecules are less strictly arranged in solution, as also noted for the pyridine solution.

The Fourier transform of EXAFS data for the copper(II) trifluoromethanesulfonate solution also shows two principal shells of low-Z scatterers around copper. In this case, the Cu^{II}–N bond distance is 1.99 Å, and the Cu$^{II}\cdots$C distance is 3.13 Å. These distances suggest that for copper(II) the Cu^{II}–N–C group is nearly

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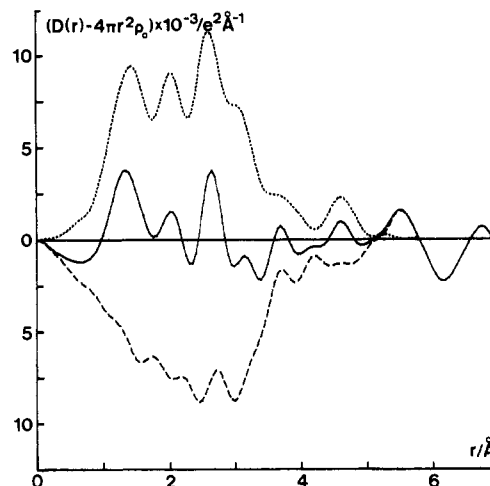(32) Csöregh, I.; Kierkegaard, P.; Norrestam; R. *Acta Crystallogr.* **1975** *31*, 314.
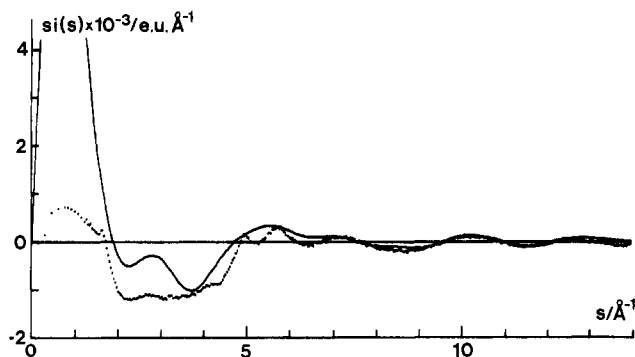
Figure 3. Experimental (dots) and calculated (solid line) intensity functions, $s(i)$ versus s, of copper(II) trifluoromethanesulfonate in acetonitrile solution. The parameters for the $Cu(CH_3CN)_4^{2+}$ complex are given in Table II, and the parameters for the trifluoromethylsulfonate ion and acetonitrile are taken from the literature, refs 30 and 36.

linear. The expected two acetonitriles completing the Jahn–Teller distorted solvate are not observed in the Fourier transform. This is, however, not surprising since the axial bonds are often not observed in EXAFS studies of Jahn–Teller distorted complexes,[33-36] particularly in room temperature measurements.

Dimethyl Sulfoxide Solutions. The Fourier transform of the EXAFS data for the copper(II) trifluoromethanesulfonate solution has two shells of scatterers. These can be fitted with Cu^{II}–O at 1.98 Å and Cu^{II}–S at 3.08 Å. From these, the Cu^{II}–O–S angle is calculated to be $123 \pm 10°$, which is consistent with that expected for oxygen-coordinated dimethyl sulfoxide complexes to fairly soft metal acceptors.[37] The expected axially coordinated dimethyl sulfoxide molecules are not observed.

The copper(I) solution was unfortunately partially oxidized to copper(II). The main peak in the Fourier transform of this solution is very broad and asymmetric, suggesting that it contains two different Cu–O distances, corresponding to the copper(I) and copper(II) species. The refinements of experimental data have been made using this assumption. By using the parameters from the dimethyl sulfoxide solvated copper(II) ion, see above, the Cu^I–O and Cu^I–S distances are found to be 2.09 and 3.18 Å, respectively, for the tetrakis(dimethyl sulfoxide)copper(I) ion. The uncertainty in the distances in the dimethyl sulfoxide solvated copper(I) ion is considerably larger than in the other structures in this study. The calculated Cu^I–O–S angle of $123 \pm 10°$ appears however to be close to that found in the copper(II) dimethyl sulfoxide solvate.

X-ray Scattering Study of $Cu(CH_3CN)_4^{2+}$. The reduced intensity curve, $i_{obs}(s)$ multiplied by s versus s is given in Figure 3. The corresponding electronic radial distribution function, RDF, $D(r) - 4\pi r^2 \rho_0$, obtained by a Fourier transformation, is given in Figure 4. Six peaks are found within 5 Å in the RDF. The peaks at 1.5, 2.6, and 3.6 Å correspond to interatomic distances in acetonitrile and the trifluoromethanesulfonate ion. The parameters for these intramolecular distances have been taken from the literature[32,38] and have not been further refined. The three peaks at 2.0, 3.1, and 4.6 Å correspond to the Cu–N, Cu–C1, and Cu–C2 distances, respectively. The least-squares refinements on the Cu–N and Cu–C1 distances gave 1.99(1) and 3.12(1) Å, respectively. The Cu–C2 distance could not be refined and was set to 4.61 Å. The experimental and the calculated intensity functions given in Figure 3 are in good agreement. The refined parameters used in the theoretical model are given in Table II.

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Figure 4. $D(r) - 4\pi r^2 \rho_0$ function and the calculated peak shape for the copper(II) trifluoromethanesulfonate acetonitrile solution with the same parameters as in Figure 3: Experimental curve (solid line), theoretical (dotted line), and the difference (dashed line).

Table I. Composition of the Copper Solutions Studied by EXAFS in mol dm^{-3}

solution	Cu(I)	Cu(II)	CF$_3$SO$_3^-$	ClO$_4^-$	solvent
Cu$^+$ in dimethyl sulfoxide	0.008	0.012	0.020		13.92
Cu^{2+} in dimethyl sulfoxide		0.50	1.00		13.30
Cu$^+$ in acetonitrile	0.20			0.20	18.8
Cu^{2+} in acetonitrile[a]		1.00	2.00		17.9
Cu$^+$ in pyridine	0.18			0.18	12.1
Cu$^+$ in tetrahydro-thiophene	1.21			1.21	10.4

[a] This solution has also been examined by means of large-angle X-ray scattering.

Table II. Intramolecular Distances (Å) in Copper(I) and Copper(II) Solvates Determined by EXAFS and LAXS[a]

solution	Cu–O	Cu–S	Cu–N	Cu–C$_1$	Cu–C$_2$
Cu((CH$_3$)$_2$SO)$_4^+$ in dimethyl sulfoxide	2.09(3)	3.18(5)			
Cu((CH$_3$)$_2$SO)$_4^{2+}$ in dimethyl sulfoxide	1.98(1)	3.08(3)			
Cu(CH$_3$CN)$_4^+$ in acetonitrile			1.99(1)	3.01(2)	4.41(4)
Cu(CH$_3$CN)$_4^{2+}$ in acetonitrile			1.99(1)	3.13(2)	4.59(4)
Cu(CH$_3$CN)$_4^{2+}$ in acetonitrile[b]			1.99(1)	3.12(1)	4.61
Cu(C$_5$H$_5$N)$_4^+$ in pyridine			2.06(1)	3.0(1)	
Cu(C$_4$H$_8$S)$_4^+$ in tetrahydrothiophene	2.30(1)				

[a] Values in parentheses are estimated uncertainties in the last digit as determined from fits to crystallographically characterized complexes (EXAFS) or from the statistical uncertainty (LAXS). [b] Structural parameters from LAXS; all other parameters from EXAFS.

Discussion

The structures of the tetrakis(acetonitrile)copper(I) and tetrakis(pyridine)copper(I) ions are almost identical in solid state and in solution, with tetrahedrally coordinated copper(I) in both cases. The outer shell bond lengths (Table II) suggest that the coordinated solvent molecules are not as strictly arranged in solution as in the solid state. For both species, the Cu–N bond distances in the solid and in solution are identical within the limits of uncertainty. Thermodynamically, the copper(I) ion is more strongly solvated in pyridine than in acetonitrile.[8] In spite of this, the Cu–N bond distance is 0.05 Å shorter in the acetonitrile solvate than in the pyridine solvate. This may be due to a less expanded electron cloud on the acetonitrile nitrogen, which allows a closer approach in spite of weaker bonding.

Table III. Bond Distances in Copper(I) and Copper(II) Solvates (Å), the Difference in Bond Distances between Copper(I) and Copper(II) (Å), and the Disproportionation Constant of Copper(I) in Water, Dimethyl Sulfoxide, Acetonitrile, and Pyridine

solvent	$d(Cu^I–X)$	$d(Cu^{II}–X)$	$d(Cu^I–X) – d(Cu^{II}–X)$	$\log K_D$
water		1.99[a]		+6.0
dimethyl sulfoxide	2.09	1.98	0.11	+0.3
pyridine	2.05	2.01[b]	0.04	–14.0
acetonitrile	1.99	1.99	0.00	–21.0

[a] Reference 42. [b] Solid state; ref 31 and this work.

Dimethyl sulfoxide can coordinate metal ions via its oxygen or sulfur atom. Typically, soft metal ions such as platinum(II) and palladium(II) coordinate dimethyl sulfoxide via the sulfur atom while more hard metal ions coordinate via the oxygen atom. The present study clearly shows that dimethyl sulfoxide coordinates to copper(I) via its oxygen atom, most probably in a tetrahedral fashion. This is supported by the high value of K_D in dimethyl sulfoxide; see Table III. K_D for copper(I) in sulfur-donating solvents should be very small, certainly less than 10^{-20} M^{-1}. Previous studies on dimethyl sulfoxide solvates of the softer d^{10} acceptors silver(I) and mercury(II) show coordination via oxygen and high coordination numbers.[18,39] It is therefore reasonable that the harder copper(I) behaves in the same way.

Copper(I) coordinates four tetrahydrothiophene molecules, most probably in a tetrahedral fashion, with copper(I) very much stabilized over copper(II) in THT solution. This stabilization is in fact so strong that copper(II) is spontaneously reduced by the solvent to copper(I). It is therefore impossible to determine the K_D value for copper(I) in THT. This value must however be extremely small, most probably smaller than the K_D value found in acetonitrile. The Cu–S bond distance which we obtained in THF is slightly shorter than those found in other complexes with four sulfur atoms coordinated to copper(I),[23-25,40,41] but significantly longer than expected for a trigonal complex.[28]

The structures of the dimethyl sulfoxide and acetonitrile solvated copper(II) ions have been determined by EXAFS, and the latter also by LAXS. These studies showed that copper(II) coordinates four solvent molecules strongly, most probably in a square-planar fashion. It was not possible to find the expected elongated axially-coordinated solvent molecules. Previous studies on hydrated Jahn–Teller distorted transition metal ions have shown that it is hard to establish the axially solvated solvent molecules, at least not with any accuracy.[33,36,42,43] The dimethyl sulfoxide solvated copper(II) ion has a Cu–O bond distance of 1.98(1) Å and a Cu–S distance of 3.08(3) Å, giving a Cu–O–S angle of approximately 123°, typical for dimethyl sulfoxide complexes with soft and intermediate soft metal ions.[37]

The results of the structure determinations of the tetrakis-(acetonitrile)copper(II) complex in acetonitrile solution by EXAFS and LAXS techniques are in very good agreement. The Cu^{II}–N(CH₃CN) bond distance of 1.99 Å is the same as in the tetrahedral $Cu(CH_3CN)_4^+$ complex. The Cu⋯C bond distance suggests that the acetonitrile molecules are linearly coordinated with a Cu–N–C angle of about 180°.

The difference in copper–solvate bond distances for copper(I) and copper(II) is strongly dependent on the solvating properties
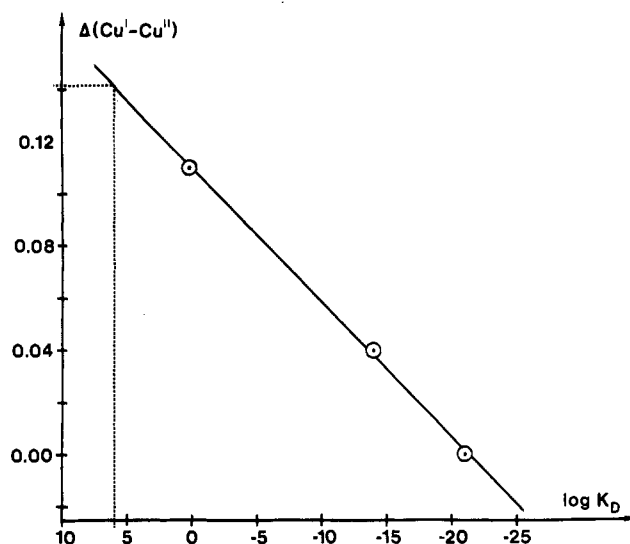
Figure 5. Relationship between the logarithm of the disproportionation constant of copper(I) and the difference in bond distance between copper-(I) and copper(II) solvates in dimethyl sulfoxide, pyridine, and acetonitrile. The dashed line denotes the expected difference in bond distance of the hydrated copper(I) and copper(II) ions.

of the solvent towards the different kinds of electron acceptors that copper(I) and copper(II) represent. In particular, the bond distances determined in this study can be correlated to the disproportionation constants of copper in the corresponding solvents, as shown in Table III and Figure 5. The difference in bond distances is found to be a linear function of the log of the disproportionation constant, K_D. Acetonitrile solvates the univalent coinage metal ions especially well while it solvates divalent ions poorly.[6,44] This is reflected in a very small K_D value and by the fact that the Cu^I–N and Cu^{II}–N bond distances in the acetonitrile solvates are the same. Dimethyl sulfoxide does not show this specific solvation of a certain group of electron acceptors, and as an oxygen donor, the harder copper(II) is preferred over copper(I). This preference for copper(II) is also seen in the fairly large K_D value, 2 M^{-1}, and the large difference between the copper-(I) and copper(II) solvate bond distances. If the data in Figure 5 are extrapolated to the K_D value for water, 10^6 M^{-1}, the difference in Cu–O bond distance between the copper(I) and copper(II) hydrates is predicted to be approximately 0.14 Å. The structure of the tetraaquacopper(I) ion, which is impossible to determine directly because it exists only in low concentrations in the presence of a large excess of copper(II), is thus proposed to consist of four water molecules coordinated to copper(I) in a tetrahedral configuration with Cu–O distances of ca. 2.13 Å.

Supplementary Material Available: Figures S1–S4 showing k^3-weighted EXAFS spectra for each of the samples studied (4 pages). Ordering information is given on any current masthead page.

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