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Structure of Jahn–Teller distorted solvated copper(II) ions in solution, and in solids with apparently regular octahedral coordination geometry†

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Regular octahedral coordination has been reported for some copper(II) complexes in the solid state on the basis of crystallographic studies, *e.g.* hexaaquacopper(II) bromate, $[Cu(OH_2)_6](BrO_3)_2$, hexaaquacopper(II) hexafluorosilicate, $[Cu(OH_2)_6]SiF_6$, and hexakis(pyridine-1-oxide)copper(II) perchlorate, $[Cu(ONC_5H_5)_6](ClO_4)_2$. These results are not consistent with the elongated octahedral configuration expected from the Jahn–Teller theorem for the d^9 copper(II) ion nor, in some cases, with results from electron spin resonance studies. The present lattice-independent EXAFS study confirms that the local structure in the copper(II) complexes mentioned above is, in all cases, consistent with a Jahn–Teller induced elongation. Mean equatorial and axial Cu–O bond distances of 1.96(1) and 2.32(2) Å, and 1.95(1) and 2.27(3) Å, were obtained for the hexaaquacopper(II) ions in the bromate and hexafluorosilicate salts, respectively. For the hexakis(pyridine-1-oxide)copper(II) perchlorate only the equatorial mean Cu–O bond distance of 1.96(1) Å could be observed. Evidently, there is orientational disorder of the tetragonally elongated octahedral complexes resulting in too high crystallographic space group symmetry and copper sites in apparently regular coordination geometry. For the hydrated copper(II) ion in aqueous solution, five- and six-coordinated models with different geometries have been evaluated by means of EXAFS and large angle X-ray diffraction (LAXS) data. The combined results are consistent with a Jahn–Teller elongated octahedral configuration with $Cu–O_{eq}$ 1.95(1) Å, $Cu–O_{ax}$ 2.29(3) Å, and a distinct second hydration sphere with about eight water molecules and a mean $Cu \cdots O_{II}$ distance of 4.17(3) Å. In dimethylsulfoxide solution EXAFS and LAXS methods show the solvated copper(II) ions to have mean equatorial and axial Cu–O bond distances of 1.96(1) and 2.24(2) Å, respectively. As a model compound for the EXAFS studies, the crystal structure of hexakis(dimethylsulfoxide)copper(II) perchlorate dimethylsulfoxide (1/2), $[Cu(OS(CH_3)_2)_6](ClO_4)_2{\cdot}2(CH_3)_2SO$, was determined.

Introduction

Six-coordinated copper(II) complexes are found in a large number of crystal structures.[1,2] Generally, these complexes display octahedral coordination geometry with a tetragonal elongation along a four-fold axis. Theoretical consideration of how six ligand atoms influence the electronic structure of the d^9 copper(II) ion, shows that certain deformations become more stable than the regular octahedral configuration.[3] For a free hexa-coordinated complex, as for a solvated copper(II) ion in solution, the Jahn–Teller theorem predicts, in the O_h point group, strong vibronic coupling between electronic and nuclear motion conveyed by normal vibrational modes belonging to the E_g symmetry species. The nuclear motion in the mean field of the electrons can be described by an adiabatic (without mixing of different electronic states) potential energy surface with three equivalent energy minima symmetrically distributed around the energy maximum at the origin corresponding to the regular octahedral configuration.[3] The minima occur for tetragonal displacements of the nuclei along the three four-fold axes of the octahedral configuration, leading to two longer axial and four shorter equatorial bond distances. Interconversion with pulsating motions of the ligand atoms takes place between the three differently oriented elongated configurations with a rate depending on the depth of the corresponding minima. There is also a weak correlation between the elongation and strength of the vibronic coupling.[3]

In order to experimentally observe the Jahn–Teller distorted nuclear configurations in such fluxional behaviour, the time of the physical event used in the measurement must be shorter than the lifetime of the system in one of the equivalent minima, otherwise the result may be an averaged apparently undistorted configuration.[3] However, diffraction and also EXAFS events are on a much shorter time scale than the vibrational motions. Thus, from a crystal structure determination an average of the instantaneous atomic *positions* should result provided that the correct space group is used, while from the lattice-independent EXAFS and large angle X-ray scattering techniques a weighted average of the instantaneous interatomic *distances* can be obtained.

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† Electronic supplementary information (ESI) available: fractional atomic coordinates and interatomic bond distances and angles of **6**; the Fourier transforms and the fit of the modelling; crystallographic data for **7**; the fit and the individual contribution of the different scattering paths of the EXAFS data; the normalised absorption edges of the studied samples; the molecular structure of copper(II) complexes in **7**. See http://www.rsc.org/suppdata/dt/b2/b200698g/

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In the solid state, crystal field effects, co-operative distortions and bonding interactions with the second shell may perturb the position and depth of the minima in the potential energy surface and quench the dynamics of the pulsating motions between different elongated configurations. A strong external influence may distort the geometry to such an extent that the internal Jahn–Teller effect becomes hidden.[3] Minor perturbations often result in a preferred direction, localising the elongation to the deepest well of the potential energy surface.

From crystallographic studies some six-coordinated copper(II) complexes have been reported to have regular,[4–16] or even compressed octahedral coordination geometry.[17–20] In a few cases the diffraction patterns then show a high symmetry space group, cubic or hexagonal, with regular octahedral copper(II) complexes for the ligands water,[4–6] pyridine-1-oxide,[7–11] octamethylpyrophosphoramide,[12] ethylenediamine,[13] nitrite,[14,15] and tris(2-pyridyl)methane.[16] However, electron spin resonance (ESR) studies indicate that for some of these compounds the octahedral configuration around copper(II) is actually tetragonally elongated with a strong vibronic coupling.[9,11,16–22]

Previously, EXAFS studies have been performed on four solid compounds for which an anomalous copper(II) coordination geometry had been reported from crystallographic studies.[16,23,24] Tris(ethylenediamine)copper(II) sulfate, $[Cu(en)_3]SO_4$, was reported with two different structures, at room temperature with six Cu–N bond distances of 2.15 Å in a regular octahedron, and at 10 K in a compressed octahedron with four Cu–N bonds at 2.22 Å and two at 2.05 Å.[13,25] Likewise, potassium lead(II) hexanitritocuprate(II), $K_2PbCu(NO_2)_6$, appeared at 295 K as a regular octahedron with Cu–N bond distance 2.11 Å,[15] and axially compressed at 193 K with Cu–N 2.06 and 2.16 Å.[26,27] Bis(tris(2-pyridyl)methane)copper(II) nitrate, was reported to be a regular octahedron at both 173 and 285 K,[16] and octa(3-chloroanilinium)hexachlorocuprate(II) tetrachloride an axially compressed octahedron with Cu–Cl 2.227 and 2.606 Å.[28] However, the EXAFS studies showed that the local structure around copper(II) in all four compounds is indeed a tetragonally elongated octahedron. For $[Cu(en)_3]SO_4$, the Cu–N equatorial and axial bond distances were found to be 2.04 and 2.28 Å at room temperature, and 2.06 and 2.34 Å at 10 K, respectively.[23] For $K_2PbCu(NO_2)_6$ and bis(tris(2-pyridyl)methane)copper(II) nitrate the corresponding bond distances were 2.04 and 2.32 Å,[23] and 2.04 and 2.25 Å.[16] In the octa(3-chloroanilinium)hexachlorocuprate(II) tetrachloride the Cu–Cl bond distances were determined as 2.28, 2.38 and 2.83 Å.[24]

Some other crystal structures have been reported with anomalous coordination geometry. The hydrated copper(II) ion in hexaaquacopper(II) bromate, $[Cu(H_2O)_6](BrO_3)_2$, described in the cubic space group $Pa\bar{3}$, appears to have six Cu–O bond distances at 2.079 Å.[6] The crystal structure of hexaaquacopper(II) hexafluorosilicate shows that copper(II), in one of the four crystallographically independent sites, seems to coordinate six water molecules in a regular octahedron with a Cu–O bond distance of 2.074 Å, while the other three hydrated copper(II) ions display Jahn–Teller distortion with Cu–O bond distances of 1.969, 1.970 and 2.368 Å.[4] Later, a more precise low temperature study was reported.[5]

During the preparation of pyridine-1-oxide complexes with copper(II) perchlorate two different compounds may crystallise, light green hexakis(pyridine-1-oxide)copper(II) perchlorate and dark green tetrakis(pyridine-1-oxide)copper(II) perchlorate. In the latter compound the crystal structure shows copper(II) to coordinate four pyridine-1-oxide molecules in square-planar fashion with Cu–O bond distances of 1.92 and 1.93 Å, with no atoms within bonding distance in the axial positions.[29] The hexakis(pyridine-1-oxide)copper(II) complex in the solid perchlorate and tetrafluoroborate salts is reported to have regular octahedral coordination with mean Cu–O bond distances of 2.086 and 2.088 Å, respectively.[7] These compounds are isostructural with a series of hexakis(pyridine-1-oxide)metal(II) perchlorates crystallising in the hexagonal space group $R\bar{3}$, allowing high symmetry.[7–11,30–32] The nitrate salt, crystallising in a monoclinic space group, has a Jahn–Teller distorted structure of the hexakis(pyridine-1-oxide)copper(II) complex with equatorial Cu–O bond distances of 1.954 and 1.970 Å, and long axial ones at 2.478 Å.[33]

A dynamical average of Jahn–Teller distortions without the preferred orientation of the elongation has been proposed as an explanation for the apparently regular octahedral structures observed for some copper(II) complexes in the solid state.[4–16] However, even well-determined crystal structures do not show obviously enlarged temperature factors for the coordinated ligand atoms.[5,13] In some cases, crystal field and lattice effects are thought to cause the anomalous structures. For example, a compressed structure of the $[CuF_6]^{4-}$ entities in $KCuAlF_6$ has been confirmed by EXAFS with bond lengths of 1.88 (×2) and 2.12 (×4) Å.[34] One purpose of the present study was to investigate whether lattice and packing forces can actually suppress the Jahn–Teller effects to make the structures regular, or if the anomalous crystal structure results are due to well-disguised orientational disorder. For that purpose, the hexaaquacopper(II) ions in the bromate and hexafluorosilicate salts, and the hexa- and tetra-kis(pyridine-1-oxide)copper(II) perchlorates,[4–11] were studied by EXAFS methods to reveal the instantaneous local structure around the copper(II) ions.

Another aim was to study the structure of solvated copper(II) ions in solution, without static external perturbance of the potential surface. It has been shown by EXAFS methods that the coordination number of copper(II) in liquid ammonia is probably five in a square pyramidal configuration, with four Cu–N bond distances of 2.00 Å and one axial, 2.19 Å.[35] Recently, it has been argued from a molecular dynamics study, supported by neutron diffraction results, that the Jahn–Teller effect for the hydrated copper(II) ion in aqueous solution would favour a five-fold coordination over an elongated octahedral one.[36] Previously, theoretical *ab initio* calculations have shown that for the pentahydrated clusters around divalent transition ions of the third period, the ligand field stabilisation energy is largest for the copper(II) ion, and that the difference in total energy between the isolated penta- and hexa-hydrated copper(II) clusters is small.[37] This is probably also the reason for the extremely fast rate of water exchange observed in aqueous solution, with a dissociative mechanism acting over a five-coordinated square pyramidal intermediate species.[37] Considering that ammonia is a much more strongly coordinating ligand than water,[38] it is not surprising that penta-coordination could be favoured in liquid ammonia, but the arguments for a similar coordination geometry being the most stable in water are not convincing.

The axial bond distances in Jahn–Teller distorted copper(II) solvates in solution are difficult to determine accurately.[39] In the current study the structures of the hydrated and the dimethylsulfoxide solvated copper(II) ions have been determined in solution by means of large angle X-ray scattering (LAXS) and EXAFS, attempting to obtain reliable axial bond distances. Contributions from distances with high Debye–Waller factors, *e.g.* the axial Cu–O bonds, are less damped in the LAXS intensity function than in the EXAFS oscillations, while short well-defined distances are normally determined with higher accuracy by EXAFS.[40] In order to obtain model compounds for the EXAFS study of the dimethylsulfoxide solvated copper(II) ion, the crystal structure of hexakis(dimethylsulfoxide)copper(II) perchlorate bis(dimethylsulfoxide) has been determined. It is of special value to compare XAFS spectra from solutions with solids containing discrete solvated ions, since not only the EXAFS part but also the edge structure and the multiple scattering features are largely determined by the local surrounding of the absorbing atoms, and can support or reject similar coordination geometry in such cases.

Table 1 Copper(II) solutions studied by EXAFS and LAXS[a]

Sample	$[Cu^{2+}]$	$[ClO_4^-]$	[Solvent]	ρ/g cm^{-3}	μ/cm^{-1}	Method
Cu^{2+}/water	0.50	1.10	51.3	1.065	3.27	EXAFS
Cu^{2+}/water	2.00	4.10	46.8	1.377	9.48	LAXS
Cu^{2+}/Me_2SO	0.44	0.88	12.78	1.140	6.26	EXAFS
Cu^{2+}/Me_2SO	0.44	0.88	12.78	1.140	6.26	LAXS

[a] Concentration in mol dm^{-3}, density ρ, linear absorption coefficient μ for Mo-Kα radiation.

Experimental

Sample preparations

Hexaaquacopper(II) hexafluorosilicate, $[Cu(H_2O)_6]SiF_6$, 1. Prepared by dissolving copper(II) hydroxide carbonate, $Cu_2(OH)_2CO_3$, in aqueous hydrogen hexafluorosilicate(IV) until saturation at room temperature. The solution was filtered, and the desired crystals were obtained after storage in a refrigerator. The unit cell parameters determined using a single crystal mounted on a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator, using Mo-Kα (λ = 0.71073 Å) radiation,[41] were in very good agreement with those reported in the crystallographic studies.[4,5] If precipitation occurs above 50 °C tetraaquacopper(II) hexafluorosilicate, $Cu(H_2O)_4SiF_6$, forms instead.

Hexaaquacopper(II) bromate, $[Cu(OH_2)_6](BrO_3)_2$, 2. Prepared as described previously.[6] The unit cell parameters, from a single crystal, were found to be in excellent agreement with those reported in the crystal structure determination.[6]

Hexakis(pyridine-1-oxide)copper(II) perchlorate, $[Cu(ONC_5H_5)_6](ClO_4)_2$, 3. Prepared as described elsewhere.[7] However, during the recrystallization a mixture of light and dark green crystals were obtained. These were shown, by determination of the unit cell parameters, to be **3** and tetrakis(pyridine-1-oxide)copper(II) perchlorate, **4**, respectively.[7,29]

Hexakis(dimethylsulfoxide)copper(II) perchlorate, $[Cu(OS(CH_3)_2)_6](ClO_4)_2$, 5. Prepared by dissolving 0.01 mol hexaaquacopper(II) perchlorate (G. F. Smith) in a minimum amount of dry acetone. After addition of 0.06 mol 2,2-dimethoxypropane (Fluka) the solution was shaken for 2 hours. 0.06 mol dimethylsulfoxide (Fluka) was then added and the resulting mixture was shaken for another 1/2 hour. On cooling in the freezer crystals formed which were recrystallized from dry acetone. The copper(II) content, analysed with EDTA titration using Murexide as indicator,[42] was consistent with hexakis(dimethylsulfoxide)copper(II) perchlorate. This compound was used to prepare the dimethylsulfoxide solution of copper(II) perchlorate. Recrystallization of hexakis(dimethylsulfoxide)copper(II) perchlorate in freshly distilled dimethylsulfoxide resulted in formation of hexakis(dimethylsulfoxide)copper(II) perchlorate bis(dimethylsulfoxide), $[Cu(OS(CH_3)_2)_6](ClO_4)_2\cdot 2(CH_3)_2SO$, **6**. When the concentrated copper(II) perchlorate solution was stored in a vessel covered by parafilm in the refrigerator the compound hexakis(dimethylsulfoxide)copper(II) bisaquatetrakis(dimethylsulfoxide)copper(II) perchlorate, $[Cu(OS(CH_3)_2)_6][Cu(OS(CH_3)_2)_4(OH_2)_2](ClO_4)_4$, **7**, precipitated. This compound crystallises in the triclinic space group $P\bar{1}$ with a = 11.310(5), b = 12.507(5), c = 12.881(5) Å, α = 62.729(9), β = 67.7066, γ = 85.391(9)°. Attempts to reproduce the preparation of this compound for a complete crystal structure determination (*cf.* Tables S3 and S4, ESI) were not successful. The composition of the solutions studied by LAXS and EXAFS is given in Table 1.

EXAFS data

The Cu K-edge EXAFS measurements were performed at Stanford Synchrotron Radiation Laboratory (SSRL), USA. SSRL operates at 3.0 GeV and a maximum current of 100 mA. The EXAFS station at the wiggler beam line 4-1 was equipped with a Si[220] double crystal monochromator. The solids and the aqueous copper(II) solution were measured in transmission mode, while fluorescence detection was used for the highly absorbing dimethylsulfoxide solution. Internal calibration was made with a copper metal foil, and higher order harmonics were discarded by detuning the second monochromator crystal to 50% of maximum intensity at the end of the scans. The treatment and model fitting of the EXAFS data were carried out using the EXAFSPAK and WinXAS program packages,[43,44] using standard procedures for pre-edge subtraction and spline removal.[45] The resulting EXAFS functions were curve-fitted by calculated model functions using *ab initio* calculated EXAFS phase and amplitude parameters from FEFF6.[46]

The standard deviations given for the refined parameters in Tables 2 and 3, were obtained from k^3 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_o value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ±0.01 to 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.

Large angle X-ray scattering (LAXS) data

The scattering from the free surface of the aqueous and dimethylsulfoxide solutions of copper(II) perchlorate was measured with a large angle θ–θ goniometer, as described previously.[47,48] Intensity data were collected in the range $1 < \theta < 65°$ using Mo-Kα radiation, λ = 0.7107 Å, following the same procedure as described elsewhere.[48]

The experimental intensities were corrected for absorption[49] and polarisation, and normalised to a stoichiometric unit of volume corresponding to one copper atom. Corrections for multiple scattering were necessary due to the low absorption (Table 1).[50] After subtraction of the structure-independent coherent and Compton scattering, the remaining structure-dependent intensity function $i(s)$ was Fourier-transformed to obtain a modified radial distribution function (RDF), expressed in the form $D(r) - 4\pi r^2\rho_o$.[51] Minor spurious peaks below 1.2 Å in the RDFs were removed by a Fourier back-transformation procedure,[52] to align the intensity function before fitting the model functions. The KURVLR program[50] was used for the data correction and treatment procedures, while the STEPLR program[53] was used for least-squares refinements of model parameters by comparing calculated intensity contributions for distinct interatomic interactions with the experimental reduced intensities for s-values >4.5 Å^{-1} ($s = (4\pi/\lambda)\sin\theta$).

The model used includes interatomic interactions between the copper(II) ion and the solvating ligands, interactions within the solvent molecules, in the case of water also the aqueous

Table 2 EXAFS model parameters for solvated copper(II) ions in the solid state and in solution[a]

Sample/colour	Path[b]	n	d/Å	σ/Å	Δk/Å^{-1}	ΔE_o/eV	S_o^2
2	Cu–O$_{eq}$	4	1.963(2)	0.069(1)	2–14	−10.2(4)	0.67(2)
Light-blue	Cu–O$_{ax}$	2	2.32(2)	0.17(1)			
	MS[b]	3 × 4	3.89(2)	0.12(1)			
1	Cu–O$_{eq}$	4	1.954(2)	0.069(3)	2–13	−10.2(5)	0.80(2)
Light-blue	Cu–O$_{ax}$	2	2.27(2)	0.16(1)			
	MS[b]	3 × 4	3.90(2)	0.08(2)			
3	Cu–O$_{eq}$	4	1.964(2)	0.066(1)	2–13	−12.1(3)	0.79(1)
Light-green	Cu · · · N	4	2.849(4)	0.080(3)			
	Cu–O–N	8	3.078(12)	0.081(8)			
	MS[b]	3 × 4	3.88(2)	0.10(1)			
7	Cu–O$_{eq}$	4	1.935(2)	0.0068(2)	2–13	−12.4(4)	1.05(3)
Dark-green	Cu · · · N	4	2.824(6)	0.085(3)			
	Cu–O–N	8	3.022(25)	0.10(2)			
	MS[b]	3 × 4	3.85(4)	0.13(2)			
4	Cu–O$_{eq}$	4	1.947(2)	0.066(1)	2–13	−7.1(5)	0.99(4)
Light-blue	Cu–O$_{ax}$	2	2.25(3)	0.18(3)			
	Cu · · · S	4	3.083(4)	0.087(3)			
	Cu–O–S	8	3.28(2)	0.10(2)			
	MS[b]	3 × 4	3.93(3)	0.11(2)			
Cu^{2+} in DMSO	Cu–O$_{eq}$	4	1.950(2)	0.065(2)	2–12.5	−9.6(4)	0.84(2)
Solution/Light-blue	Cu · · · S	4	3.064(4)	0.092(2)			
	Cu–O–S	8	3.31(3)	0.10(2)			
	MS[c]	3 × 4	3.91(2)	0.13(2)			

[a] Model parameters: coordination number (n), distance (d), disorder parameter σ in Debye–Waller factor $\exp(-2k^2\sigma^2)$, refinement range Δk, shift in E_o, amplitude reduction factor S_o^2. Standard deviations are given as estimated from the least squares procedure. [b] Paths: single back-scattering from a square-planar (equatorial) or axial unit in an elongated (Jahn–Teller distorted) octahedron. [c] The linear multiple scattering pathways, Cu–O–O and two different Cu–O–Cu–O, have been refined with the same value for their corresponding structure parameters (d, n and σ).

Table 3 EXAFS data for the hydrated copper(II) ion, $[Cu(H_2O)_n]^{2+}$, n = 5 or 6, in solution with different coordination models[a]

Model geometry	Path	n	d/Å	σ^2/Å^2	σ/Å	ΔE_o/eV	S_o^2	F
Tetragonally elongated octahedron	Cu–O$_{eq}$	4	1.953(2)	0.0067(3)	0.082(2)	−10.2(5)	0.96(4)	0.0791
	Cu–O$_{ax}$	2	2.25(3)	0.036(6)	0.19(2)			
	MS[b]	3 × 4	3.93(2)	0.012(3)	0.11(3)			
Elongated square pyramid	Cu–O$_{eq}$	4	1.952(2)	0.0068(3)	0.082(2)	−10.2(5)	0.97(3)	0.0793
	Cu–O$_{ax}$	1	2.29(3)	0.021(5)	0.15(2)			
	MS[b]	3 × 4	3.92(2)	0.012(3)	0.11(3)			
Regular square pyramid	Cu–O	5	1.950(2)	0.0062(2)	0.079(2)	−11.0(4)	0.70(2)	0.0908
	MS[b]	2 + 5	3.87(2)	0.011(3)	0.10(3)			
Trigonally elongated bipyramid	Cu–O$_{eq}$	3	1.952(2)	0.0068(3)	0.082(2)	−9.7(6)	1.24(7)	0.0807
Cu–O$_{ax}$	2	2.23(3)	0.047(10)	0.22(3)				
Cu–O–O	6	3.66(3)	0.0167(8)	0.13(1)				
MS[b]	4	4.07(2)	0.005(3)	0.07(3)				
Trigonal regular bipyramid	Cu–O	5	1.952(2)	0.0068(3)	0.082(2)	−11.2(5)	0.71(2)	0.0931
	Cu–O–O	12	3.59(2)	−0.010(2)	—			
	MS[b]	2 + 5	4.00(2)	−0.007(2)	—			

[a] Model parameters: as in Table 2 and residual factor (F), see ref. 45. [b] The linear multiple scattering pathways, Cu–O–O and different Cu–O–Cu–O, have been refined with the same value for their corresponding structural parameters (d, n and σ).

bulk structure, and within the anions. The starting model of the hydrated perchlorate ion in aqueous solution was taken from previous work.[40] The standard deviations for the refined parameters in Table 4 are based on statistical estimates from the noise level in the data, but have been increased to approximately account for the estimated additional influence of systematic errors.

Crystallography

Data were collected on a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator using Mo-Kα (λ = 0.71073 Å) radiation.[41] A hemisphere of data (1295 frames) was collected using the ω scan method (0.3° frame width). The crystal to detector distance was 5.0 cm. The first 50 frames were remeasured at the end of the data collection to check crystal and instrument stability, and showed negligible intensity decay. The structure was solved by direct methods and refined using full-matrix least-squares on F^2 by means of the SHELXTL program system.[54] Non-hydrogen atoms were treated anisotropically. The methyl hydrogen atoms were introduced in calculated ideal positions riding on their respective carbon atom.

Crystal structure determination of complex 6. $C_{16}H_{48}Cl_2O_{16}S_8Cu$, M = 887.510, triclinic, a = 9.772(4), b = 10.551(4), c = 11.563(4) Å, α = 64.237(6), β = 71.779(6), γ = 87.448(7)°, V = 1014.1(6) Å^3, T = 22 ± 2 °C, space group $P\bar{1}$ (no. 2), Z = 1, μ(Mo-Kα) = 1.137 mm^{-1}, 6389 reflections measured, 4625 unique (R_{int} = 0.0512) which were all used in the calculations. The final $wR(F^2)$ values are 0.0553 ($I > 2\sigma(I)$) and 0.1015 (all data).

CCDC reference number 177918.

See http://www.rsc.org/suppdata/dt/b2/b200698g/ for crystallographic data in CIF or other electronic format.

Table 4 LAXS model parameters for solvated copper(II) ions in aqueous (with different coordination geometries) and dimethylsulfoxide solution[a]

Sample/model	Species	Distance	*n*	*d*/Å	σ/Å	*R*-factor[b]
Cu^{2+}(aq)/Tetragonally elongated octahedron	$[Cu(H_2O)_6]^{2+}$	Cu–O_{eq}	4	1.955(5)	0.047(3)	0.0141
		Cu–O_{ax}	2	2.30(3)	0.087(5)	
		Cu ··· O_{II}	8	4.17(3)	0.13(1)	
Cu^{2+}(aq)/Elongated square pyramid	$[Cu(H_2O)_5]^{2+}$	Cu–O_{eq}	4	1.963(6)	0.047(3)	0.0151
		Cu–O_{ax}	1	2.34(2)	0.057(8)	
		Cu ··· O_{II}	8	4.18(3)	0.13(1)	
Cu^{2+}(aq)/Elongated trigonal bipyramid	$[Cu(H_2O)_5]^{2+}$	Cu–O_{eq}	3	1.935(6)	0.037(3)	0.0159
		Cu–O_{ax}	2	2.15(3)	0.087(4)	
		Cu ··· O_{II}	6	4.12(3)	0.110(5)	
Cu^{2+}(aq)/Regular square pyramid	$[Cu(H_2O)_5]^{2+}$	Cu–O_{eq}	5	1.98(1)	0.074(4)	0.0311
		Cu ··· O_{II}	10	4.19(3)	0.013(1)	
Cu^{2+}(aq)/Regular trigonal bipyramid	$[Cu(OH_2)_6]^{2+}$	Cu–O_{eq}	5	1.977(8)	0.073(2)	0.0274
		Cu ··· O_{II}	10	4.17(3)	0.013(1)	
	ClO_4^-(aq)[d]	Cl–O	4	1.450(3)	0.041(2)	
		(Cl–)O ··· O	12	3.05(4)	0.14(2)	
		Cl–(O) ··· O	12	3.68(3)	0.14(2)	
	Aqueous bulk[d]	O_w ··· O_w	2	2.88(2)	0.101(5)	
		O_I ··· O_{II}	2	2.81	0.10	
Cu^{2+}(dmso)/Tetragonally elongated octahedron	$[Cu(OSMe_2)_6]^{2+}$	Cu–O_{eq}	4	1.965(8)	0.128(6)	
		Cu–O_{ax}	2	2.25(3)	0.17(3)	
		Cu ··· S	4	3.11(3)	0.11(2)	

[a] Parameters: Interatomic distance *d*/Å, displacement parameter, σ/Å, and number of distances, *n*. [b] *R*-factor: error-square sum/Σ(data values).[2] [c] Estimated errors for least-squares refined parameters are given within brackets as standard deviations (3σ). [d] Hydrated perchlorate ion and hydrogen bonded O ··· O interactions common for all aqueous solution models.

Results and discussion

Copper(II) solvates with apparently regular octahedral coordination geometry

Hexaaquacopper(II) bromate. The EXAFS spectrum of **2** is similar to the spectrum of the aqueous copper(II) perchlorate solution, while it differs significantly from a calculated spectrum obtained by refining the amplitude reduction factor and the Debye–Waller parameters for the coordination reported in the crystal structure,[6] *cf.* Fig. 1a. The curve-fitting revealed two mean Cu–O bond distances, 1.963(2) and 2.32(2) Å, as expected for coordination of water molecules in equatorial and axial positions, respectively. The linear multiple scattering (MS) pathways at twice the Cu–O_{eq} bond distance (Cu–O–O and two different Cu–O–Cu–O) give significant contributions in the Fourier transform, while all other MS paths can be neglected. The fit of the refined model function to the experimental data, and the contribution from the individual scattering pathways, are given in Figs. 2 and S2a (ESI), respectively. The model parameters are summarised in Table 2. The EXAFS results and the similarity with the solution data show that the hydrated copper(II) ion in **2** is Jahn–Teller distorted, as proposed in a previous EPR study.[17]

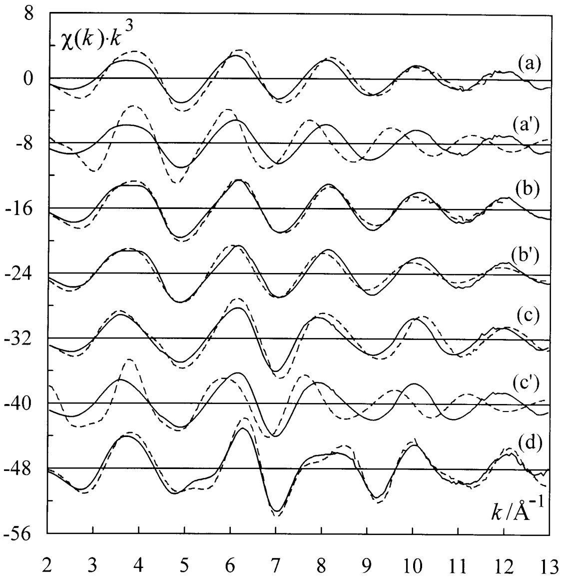

Fig. 1 Comparison of Cu K-edge EXAFS spectra of (a) **2** (solid line) and an aqueous solution of copper(II) perchlorate (dashed line); (a′) **2** (solid line) and a model spectrum based on the crystal structure reported of **2** (dashed line); (b) **1** (solid line) and an aqueous solution of copper(II) perchlorate (dashed line); (b′) **1** (solid line) and a model spectrum based on the crystal structure (dashed line); (c) **3** (solid line) and **4** (dashed line); (c′) **3** (solid line) and a model spectrum of **3** calculated from the reported crystal structure (dashed line); and (d) **5** and a dimethylsulfoxide solution of copper(II) perchlorate.

Hexaaquacopper(II) hexafluorosilicate. The EXAFS spectra of **1** and the aqueous solution of copper(II) perchlorate are very similar (Fig. 1b), while the calculated spectrum based on regular copper(II) coordination in one of the four sites, as reported in the crystal structure (refining the Cu–O Debye–Waller factor),[4,5] shows a significant phase shift. The curve-fitting revealed two mean Cu–O bond distances, 1.954(2) and 2.27(3) Å, which correspond to the equatorial and axial coordinated water molecules, respectively (Table 2). The linear multiple scattering pathways at twice the Cu–O bond distance give a significant contribution to the EXAFS function, while all other MS paths can be neglected. The fit of the curve-fitted model with separate contributions from the individual paths is displayed in Figs. 2 and S2b (ESI), respectively. The result shows that the copper atom reported to be in a site with regular octahedral symmetry, has in fact a Jahn–Teller distorted environment.

Hexakis(pyridine-1-oxide)copper(II) perchlorate. The Fourier transforms (FT) of the EXAFS spectra of **3** and **4** are significantly different and show that the mean Cu–O bond distance is shorter in the **4** (Fig. S1, ESI). Also, the calculated model spectrum based on the crystallographic structure determination of **3**,[7] differs from both experimental spectra (Fig. 1c). Curve-fitting revealed, for both compounds, four Cu–O bond distances corresponding to equatorial positions, with a significantly longer mean distance in **3** than in **4** (Table 2). The contribution to the EXAFS from the two expected axial Cu–O_{ax} bond distances in the former compound is too weak to

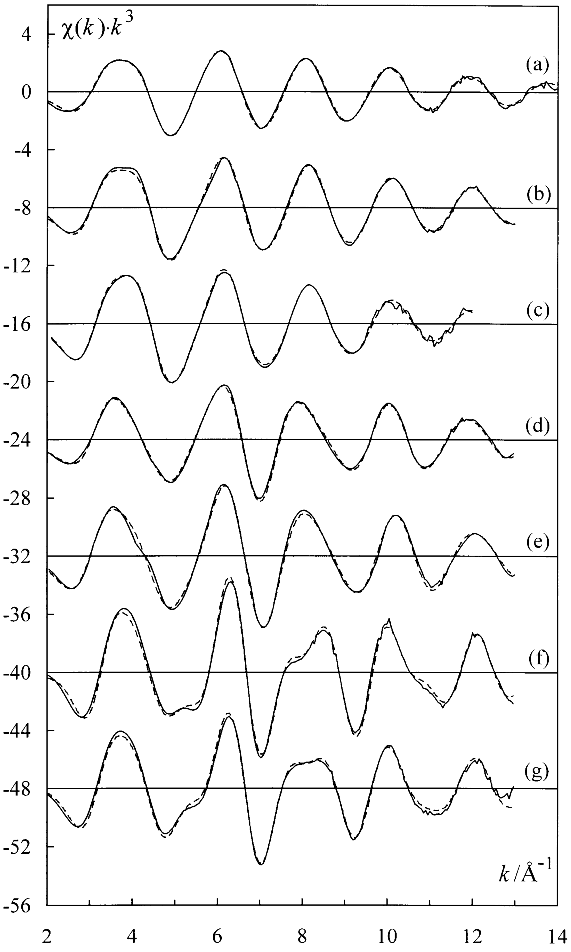

Fig. 2 The fit of the model (dashes) to the EXAFS data (solid line) of (a) **2**, (b) **1**, (c) an aqueous solution of copper(II) perchlorate, (d) **3**, (e) **4**, (f) **5** and (g) a dimethylsulfoxide solution of copper(II) perchlorate.

be observed. For both compounds four Cu ··· N distances and a three-legged Cu–O–N multiple scattering pathway could be introduced corresponding to Cu–O–N angles close to 120°. The linear multiple scattering pathways within a planar CuO_4 coordination entity at twice the Cu–O bond distance give additional significant contributions to the EXAFS, while the other possible multiple scattering paths can be omitted. The final curve-fitting results and the contribution from the individual paths are shown in Figs. 2 and S2d (ESI), respectively.

The EXAFS results show that the hexakis(pyridine-1-oxide)-copper(II) complex in the perchlorate salt is also Jahn–Teller distorted at room temperature. The high crystal symmetry and the apparent regular octahedral configuration around copper(II) in the crystal structure probably results from a fluxional dynamic change in the direction of the distortion. At low temperature the crystal structure shows the tetragonally elongated complexes to be aligned in the same direction throughout the crystal, which results in a crystal lattice with lower symmetry.[9]

The Cu–O bond distances obtained by model curve-fitting for **4** are in good agreement with the distances reported in the crystallographic study.[29]

Structure of solvated copper(II) ions in solution

1. The hydrated copper(II) ion. Pasquarello *et al.* recently proposed that the hydrated copper(II) ion is five-coordinated in aqueous solution,[36] in contradiction to the general view of a Jahn–Teller distorted octahedral configuration.[3,55] This conclusion was based on results from large angle neutron diffraction and a molecular dynamics simulation study. Second-order differences between neutron scattering data from isotopically substituted solutions were used to extract partial pair correlation functions for separate distributions of oxygen atoms and hydrogen atoms around copper. The oxygen distribution showed a single peak at Cu–O 1.96 Å with no definite signature for elongated bonds.[36] By integrating the smoothed function up to a limit of 3.02 Å a five-fold Cu–O coordination was achieved. The statistical noise in the neutron intensity data was estimated to give an error of ±0.15 in the Cu–O correlation.[36] No attempt was made to estimate systematic errors in the data treatment procedures, and the raw data were not presented. However, in neutron diffraction it is difficult to obtain the very high signal-to-noise ratio of the intensity data necessary for reliable double differences, considering *e.g.* the substantial corrections for incoherent scattering, sample container, absorption, *etc.* Also, the two types of Cu–O interactions with very different Debye–Waller factors contribute with different weights to the intensity data in the experimental momentum transfer range.

Previous experience has shown that instead of attempting to directly evaluate coordination numbers from solution diffraction and EXAFS data, the close correlation between bond distances and coordination number give more reliable results in comparisons with similar structures in the solid state.[56] In this case, the well-defined Cu–O bond distance obtained in the neutron diffraction experiment, 1.96 Å, agrees well with the four $Cu–O_{eq}$ bond distances in the present study of hexaaquacopper(II) ions, in solution as well as in distorted octahedral configurations in the solid state, while the resolution of the neutron data is not sufficient to clearly show the $Cu–O_{ax}$ distances, expected at about 2.3 Å.

A problem ever present with molecular dynamics simulations is how to represent covalent bonding and polarisation of the ligands. A crystallographic electron difference density study on the hexaaquacopper(II) ion in the Tutton's salt, $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, shows significant differences in the Cu–O bonding covalency.[57] The closer the oxygen atom approaches the metal nucleus the less developed its lone pair was found to be. Moreover, the hydrogen bonding of the water ligands to the second shell was found to be important for the polarisation, and of different strength for the equatorial and axial water ligands.[58] This has also been measured by IR absorption spectroscopy on HDO water molecules coordinated to the metal ions in caesium Tutton's salts, $Cs_2[M(H_2O)_6](SO_4)_2$, M = Cu or Ni, and in aqueous copper(II) and nickel(II) solutions with a few percent added D_2O.[59] The hydrated nickel(II) ion in aqueous solution gives a single O–D stretching band corresponding to an enhanced hydrogen bond from the polarised water ligands, while the copper(II) ion gives two bands, corresponding to the unequal strength of the hydrogen bonds from the equatorial and axial water ligands. The solid Tutton's salts give a similar picture with a large splitting for the copper(II) compound between two groups of O–D stretching frequencies, which can be ascribed to the Jahn–Teller distorted structure.[59]

Transition metal, and in particular copper(II) complexes, are notoriously difficult to model with force fields, and it is difficult even with *ab initio* calculations to satisfactorily account for the Jahn–Teller energies and geometrical distortion for a hexahydrated copper(II) ion.[37,59,60] Averaged pseudo-potentials in a molecular dynamics simulation cannot describe the vibronic coupling of E-type normal vibrations, which causes the Jahn–Teller distortion in octahedral d^9 systems.[3] Spherically symmetric potentials will result in regular coordination geometries and size-dependent solvation numbers. Indeed, from the MD simulation of Pasquarello *et al.* regular square pyramidal and regular trigonal bipyramidal configurations of water molecules are proposed to be in equilibrium around the simulated copper(II) ion.[36] However, *ab initio* studies of successive hydrated clusters of the Cu^{2+} ion have indicated that at least three-body terms are needed to reasonably account for the distorted octahedral structure when simulating the hydration of the ion in solution from first-principles.[61,62] To keep the complexity of the computations at a manageable level it was found necessary to use hybrid models combining *ab initio* quantum mechanical and molecular mechanics Monte Carlo simulations.[61] Attempts to account for the directional properties of the Cu–O potential have been made with molecular dynamics simulations using a time-dependent rotation of the internal coordinate system of the hexa-hydrated copper ion,[61] or by introducing additional energy terms based on ligand-field d-orbital splitting to model the Jahn–Teller distortion in molecular mechanics simulations.[63,64]

In the current structural study we applied both LAXS and EXAFS methods on the hydrated copper(II) ion in aqueous solution. The data were modelled comparing five different geometrical configurations, Jahn–Teller distorted octahedron, regular trigonal bipyramid, trigonally elongated bipyramid, regular square pyramid, and square pyramid with the apex position elongated. A regular octahedral model was excluded since the experimentally observed Cu–O bond distance is much shorter than that expected for a regular octahedron, 2.07 Å. Also, a square-planar geometry was not considered because complexes with the square-planar CuO_4 entity without axial interactions are only formed in solution when there are steric restrictions present and the square-planar copper(II) complexes are dark green.

The LAXS radial distribution function (RDF) for a slightly acidified aqueous copper(II) perchlorate solution shows four major peaks at 1.4, 2.0, 2.9 and 4.1 Å (Fig. 3). The peak at 1.4 Å corresponds to the Cl–O bond distance within the perchlorate ion, the peaks at 2.0 and 4.2 Å originate from the Cu–O_I bond and Cu · · · O_{II} distances to the first and second hydration sphere, respectively. The 2.9 Å peak comprises contributions from hydrogen-bonded O · · · O distances in the aqueous bulk and between water molecules in the first and second hydration sphere around copper(II), and between perchlorate ions and hydrating water molecules. The shoulder at 2.3 Å corresponds to interatomic O · · · O distances within the perchlorate ion, and also to the axial Cu–O bonds.

The LAXS data have been fitted with the five different models mentioned above. The results of the refinements using these five models are summarised in Table 4. The regular square pyramidal and trigonal bipyramidal models gave significantly poorer fits than the asymmetric models with Cu–O bond distances at *ca.* 1.96 and 2.3 Å. The Jahn–Teller distorted octahedral model gives a marginally better fit than the trigonally elongated bipyramidal and elongated square pyramidal models. However, the displacement (Debye–Waller) parameter σ of the axial Cu–O bond is unrealistically small in the elongated square pyramidal model, only slightly larger than for the 0.3 Å shorter equatorial Cu–O bonds; the displacement parameter of the axial Cu–O bonds in the Jahn–Teller distorted octahedral model is more than three times larger than for the equatorial bonds, which seems reasonable (Table 4). The fit using the trigonally elongated bipyramidal model results in shorter Cu–O_{eq} and Cu–O_{ax} bond distances, which are accompanied with smaller displacement parameters than in the Jahn–Teller distorted octahedral model. The trigonally elongated bipyramidal model cannot be ruled out on the grounds of unrealistic model parameters, however, it has higher energy than both the square pyramidal and distorted octahedral models in an *ab initio* calculation.[37]

The models giving the best fit to the LAXS data are the tetragonally elongated octahedron and the trigonally elongated bipyramid. The structural parameters of the six-coordinated model are in close agreement with those obtained for hydrated copper(II) ions in solid compounds.[1,2] Least-squares refinements gave Cu–O_{eq} and Cu–O_{ax} bond distances of 1.955(5) and 2.30(3) Å, respectively, and a well-defined Cu · · · O_{II} interaction at 4.17(2) Å corresponding to a second hydration sphere hydrogen-bonded to the equatorial water ligands. For the tetragonally elongated octahedral model the fit of the calculated intensity function to the experimental intensity data, and the fit of the Fourier transform to the modified radial distribution function (RDF), with separate contributions to the RDF shown for the individual complexes, are given in Fig. 3; with corresponding fits for the other investigated models in Fig. S3 (ESI).

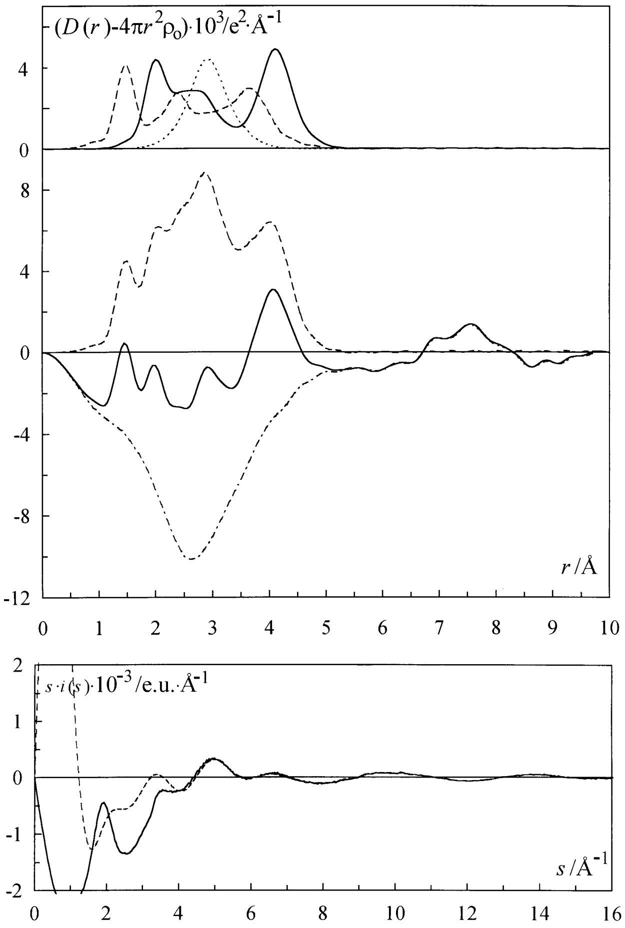

Fig. 3 Upper: LAXS modified radial distribution curves for a 2.0 mol dm^{-3} acidic aqueous solution of copper(II) perchlorate using a Jahn–Teller distorted tetragonally elongated octahedral model. Separate model contributions: the hydrated copper(II) ion with the first and second sphere (solid line), the hydrated perchlorate ion (dashed line) and O_w · · · O_w in the aqueous bulk (dotted line). Middle: Experimental RDF, $D(r) - 4pr^2r_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). Lower: LAXS structure-dependent intensity functions $s\cdot i(s)$; experimental (solid line) and calculated (dashed line).

The EXAFS data of an aqueous solution of copper(II) perchlorate, acidified with perchloric acid to avoid hydrolysis, show a strong contribution from the Cu–O bonds at *ca.* 1.95 Å, and a weaker contribution at twice the Cu–O bond distance from multiple scattering within the first coordination sphere. Curve-fitting has been performed using the same five basic geometric models as tested on the LAXS data. The curve-fitting of the six-coordinated model resulted in four equatorial Cu–O bond distances of 1.953(2) Å, O–Cu–O multiple scattering paths at 3.93(3) Å, and a weak contribution from axial Cu–O bonds at 2.25(3) Å (Table 3).

This is consistent with a recent EXAFS study of a 0.1 mol dm^{-3} $Cu(ClO_4)_2$ solution, giving the corresponding Cu–O bond distances 1.966(4) and 2.29(2) Å.[65] The data analysis was performed with another *ab initio* program, GNXAS.[66] The separate multiple scattering contributions were examined from the planar CuO_4 entity, and it was found that the quasi-linear O–Cu–O configurations give multiple scattering contributions that are enhanced due to focusing effects. The O_{eq}–Cu–O_{eq}

angle was reported to be 179 ± 2°, thus providing direct structural evidence of a distorted octahedral complex in solution.

Curve-fitting with the regular square pyramidal model gave a Cu–O bond distance of 1.950(2) Å and a multiple scattering path distance of 3.87(2) Å (Table 3); other multiple scattering paths could be neglected. This Cu–O bond distance is far too short for a regular five-coordinated CuO_5 complex, based on the ionic radius of copper(II) in five-coordination, 0.65 Å,[67] and the radius of the oxygen atom in water ligands, 1.34 Å,[68] or theoretically calculated differences in mean bond lengths.[37] The small value of the amplitude reduction factor obtained for the calculated model function indicates that the coordination number is lower than five in the first coordination shell (with Cu–O about 1.95 Å).

The fit to the experimental data with an elongated square pyramidal model gave a better fit, as good as for the Jahn–Teller distorted octahedron (Table 3). One difference in the results is a significantly lower Debye–Waller factor in the elongated square pyramidal model with only one long distance. When using a trigonally elongated bipyramidal model the large value of the amplitude reduction factor indicates a coordination number higher than three in the first coordination shell (Table 3). The multiple scattering pathways observed experimentally correspond to path distances which do not agree with those calculated by the FEFF program for a trigonal configuration around copper(II).

To summarise, the EXAFS data strongly indicate that the hydrated copper(II) ion binds four water molecules arranged in a square-plane, and that a further one or two water molecules are bound at a longer distance in aqueous solution at room temperature. Both the LAXS and EXAFS data show that regular square pyramidal and regular trigonal bipyramidal five-coordination are improbable configurations, since significantly better fits can be obtained with other models. The elongated square pyramidal configuration seems also to be less likely than the tetragonally elongated octahedral six-coordination because of the small displacement factors of the elongated Cu–O bonds, as observed in both LAXS and EXAFS data.

The contribution from interactions with a large Debye–Waller factor is less damped in the structure-dependent intensity of LAXS than in EXAFS (Fig. 4).[40,51] This allows the Cu–O bond distance to the axial water molecules of the hydrated copper(II) ion in aqueous solution to be fairly well-established from the LAXS measurements. Moreover, the second hydration sphere is clearly observed in the LAXS experiment but not detected in EXAFS, *cf.* Fig. 4. However, including the two Cu–O axial bond distances in the model results in a slightly improved fit to the EXAFS data. In the solid solvates, the coordinating axial atoms normally have somewhat smaller Debye–Waller factors than in solution, and are therefore easier to detect by EXAFS. Moreover, the results from the EXAFS and LAXS studies on the hydrated copper(II) ion in aqueous solution are in satisfactory agreement with solid state structures containing non-perturbed tetragonally elongated octahedral hexaaquacopper(II) ions.[1,2] Our results do *not* support a regular five-fold or elongated trigonal bipyramid coordination of the hydrated copper(II) ion in aqueous solution at room temperature.

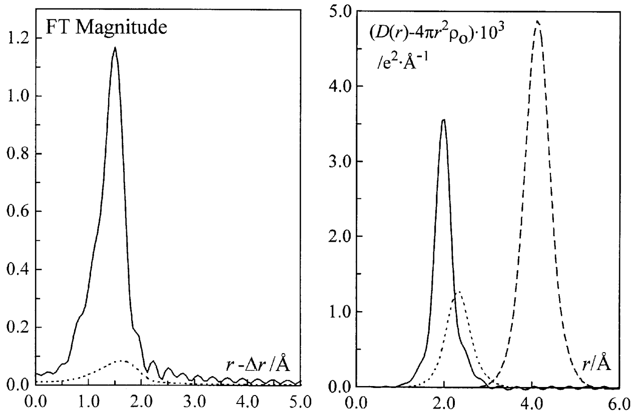

Fig. 4 The individual contribution of the Cu–O distances from EXAFS (left) and large angle X-ray scattering (right) using the refined structural parameters (Tables 3 and 4): solid line Cu–O_{eq}, dotted line Cu–O_{ax} and dashed line Cu ··· O_{II} (only observed by LAXS).

2. The dimethylsulfoxide solvated copper(II) ion. There is only one crystal structure reported for a compound containing a hexakis(dimethylsulfoxide)copper(II) ion, $[Cu(OS(CH_3)_2)_6]W_6O_{18}$, which has four short (1.964, 1.979 Å) × 2 and two long (2.372 Å) × 2 Cu–O bond distances.[69] Perchlorate is a more appropriate anion for preparation of solutions and model compounds for an EXAFS study, see Experimental section. However, despite several attempts we have not been able to prepare single crystals of the required quality for a crystallographic study of **5**. Recrystallization from dimethylsulfoxide results in compound **6**. This structure is built up of hexakis(dimethylsulfoxide)copper(II) and perchlorate ions, with two uncoordinated dimethylsulfoxide molecules in the lattice. The hexakis(dimethylsulfoxide)copper(II) ion in this compound has a distorted centrosymmetric octahedral coordination with the Cu–O bond distances 1.990, 2.080 and 2.182 Å. The structure is strongly perturbed from the normal observed tetragonally elongated Jahn–Teller distortion. Similar distributions of the bond distances for *e.g.* the Tutton's salts $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$,[58] or the Cu^{2+} doped $(ND_4)_2[Zn(D_2O)_6](SO_4)_2$ were previously observed to be temperature dependent.[70] This could be interpreted as a distribution of two energy states differing only in the orientation of the elongated hexahydrated ion in the lattice. A similar explanation with energy minima in the potential energy surface of unequal depth for different elongations, seems probable for the structure of the present hexakis(dimethylsulfoxide)copper(II) complex (Fig. 5). Fractional atomic and thermal coordinates, and the bond distances and angles are given in Tables S1 and S2 (ESI), respectively.

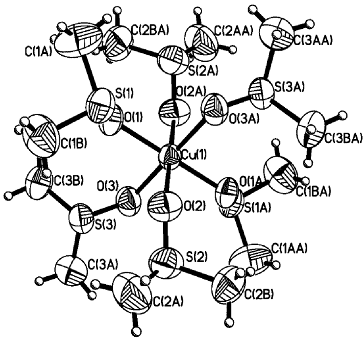

Fig. 5 The centrosymmetric hexakis(dimethylsulfoxide)copper(II) complex in the crystal structure of **6**. The distances are Cu–O(1) 1.990(4), Cu–O(2) 2.182(4), Cu–O(3) 2.083(4) Å.

The EXAFS spectra of **5** and its dimethylsulfoxide solution have many similar features, but there are also some differences (Fig. 1d). The model curve-fitting revealed similar parameters for the equatorially coordinated dimethylsulfoxide ligands for both samples. The axial Cu–O bond distance could be detected in the solid state (Table 2), but not for the dimethylsulfoxide solution. The Cu ··· S distance of the equatorial dimethylsulfoxide ligands is well-defined and contributes both *via* a single (Cu ··· S) and a three-leg (Cu–O–S) back-scattering path. The observed distances of the Cu ··· S and Cu–O–S scattering pathways both in the solid state and solution correspond to a Cu–O–S angle of about 125°. The multiple scattering at twice the Cu–O bond distance within the planar CuO$_4$ entity gives a significant contribution to the EXAFS spectra and has to be included in the curve-fitting for unfiltered data. The structural parameters refined for the hexakis(dimethylsulfoxide)copper(II) complex in the solid and of the dimethylsulfoxide solvated copper(II) ion in dimethylsulfoxide solution are summarised in Table 2.

Due to the limited solubility of **5** in dimethylsulfoxide, 0.44 mol dm^{-3}, only the Cu ··· S distance can be clearly seen in the modified radial distribution function of the LAXS study (Fig. 6). Refinement of a tetragonally elongated octahedral coordination model could be performed on the intensity data and resulted in the Cu–O$_{eq}$, Cu–O$_{ax}$ and Cu ··· S$_{eq}$ distances 1.95(1), 2.24(3) and 3.15(1) Å, respectively, which agree well with the results from the EXAFS study (Tables 2 and 3).

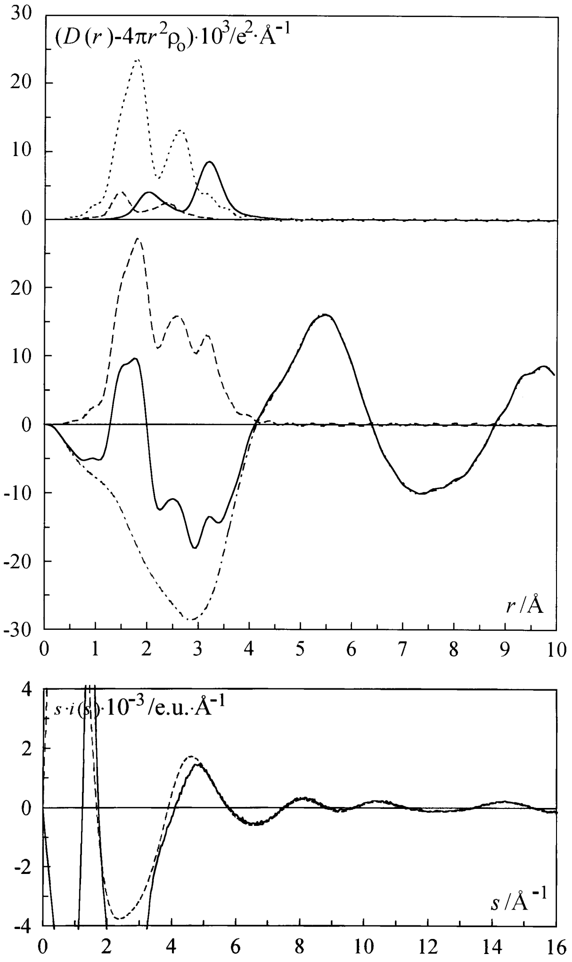

Fig. 6 Upper: LAXS modified radial distribution curves for a 0.44 mol dm^{-3} dimethylsulfoxide solution of copper(II) perchlorate. Separate model contributions: the dimethylsulfoxide solvated copper(II) ion (solid line), the perchlorate ion (dashed line) and dimethylsulfoxide (dotted line). Middle: Experimental RDF, $D(r) - 4pr^2r_o$ (solid line); sum of model contributions (dashed line); difference (dash-dotted line). Lower: Structure-dependent LAXS intensity functions $s\cdot i(s)$ (solid line); model $s\cdot i_{calc}(s)$ (dashed line).

Thus, the combined EXAFS and LAXS results show the solvated copper(II) ion to have Jahn–Teller distorted octahedral coordination in dimethylsulfoxide solution with mean equatorial and axial Cu–O bond distances of 1.96(1) and 2.24(3) Å, respectively. The Cu–O–S bond angle is about 125°, which is typical for an intermediate electron acceptor such as copper(II).[71]

Conclusions

For the solid compounds studied in this work, applying the EXAFS method for local structure determination, the structures of copper(II) complexes reported to be regular or tetragonally compressed octahedra from crystallographic studies, were found to have the usual Jahn–Teller distorted tetragonally elongated octahedral configuration.[23,24] This is also in accordance with previous ESR studies on *e.g.*, the hexaaqua- and hexakis(pyridine-1-oxide)copper(II) complexes.[9,26] It is therefore recommended that regular or tetragonally compressed octahedra obtained from crystallographic studies of the d^4 and d^9 ions chromium(II), manganese(III) and copper(II) always should be investigated further with a structural method independent of the crystal lattice, such as EXAFS.

The recent proposition that the hydrated copper(II) ion is five-coordinated in aqueous solution has been critically evaluated by means of model fitting of LAXS and EXAFS data. The results are consistent with the generally accepted tetragonally elongated Jahn–Teller distortion of the octahedral configuration, with four equatorial Cu–O bond distances at 1.954(5) Å and two axial at 2.28(4) Å, and *not* with regular five-coordination or an elongated trigonal bipyramid configuration. Also, the multiple scattering in the EXAFS studies strongly indicates a planar CuO$_4$ entity, which would rule out an elongated square pyramidal configuration. In dimethylsulfoxide solution the hexasolvated copper(II) ion is Jahn–Teller distorted, as also in **6**, although with a structure corresponding to a somewhat perturbed potential surface in the solid compound.

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