

# Solvation of Copper(II) Ions in Liquid Ammonia

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X-ray absorption fine structure (XAFS) measurements have been performed at  $-50\text{ }^{\circ}\text{C}$  on a  $0.4\text{ mol dm}^{-3}$  copper(II) nitrate solution in liquid ammonia. Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to determine the coordination number and bond distances for the solvated copper(II) ion in solution. The equatorial ammonia nitrogens are located  $2.00\text{ }\text{\AA}$  from the copper and the axial nitrogen  $2.19\text{ }\text{\AA}$  from the copper. However, it was not possible from the EXAFS analysis alone to conclude whether there was one or two axial nitrogens. Therefore, X-ray absorption near-edge structure (XANES) spectroscopy was combined with discrete variational  $X\alpha$  (DV- $X\alpha$ ) molecular orbital calculations for a series of five- and six-coordinated models to determine the coordination number and the geometry. The experimental XANES spectrum was best reproduced by a model where the copper(II) ion is pentacoordinated in liquid ammonia in a square pyramidal geometry with the copper(II) ion lifted above the average nitrogen plane.

## Introduction

The even-energy shift of the UV–visible absorption band of copper(II) in aqueous solution toward higher energy upon addition of one to four ammonia equivalents, known as the *blue shift*, has been known for a long time.<sup>1</sup> However, it was at the same time also noted that upon addition of a fifth equivalent of ammonia the absorption band shifts in the opposite direction, the so-called *pentaammine effect*.<sup>1</sup> It was early shown that the rather stable (tetraammine)copper(II) complex is converted to the pentaammine complex in highly concentrated aqueous ammonia solutions.<sup>2–4</sup> Furthermore, it was also shown that the UV–visible absorption spectrum of the copper(II) ion in the aqueous ammonia solution is but a little different from that of copper(II) in liquid ammonia.<sup>2</sup> However, it was not possible from these experiments to determine whether the coordination number of five ammonia equivalents around copper(II) could be exceeded or not in a solution.<sup>1</sup> Bjerrum maintained from these experiments that there was no evidence for a hexaammine complex and tried to prove that the maximum coordination number could not exceed five.<sup>1</sup>

The structure of copper(II) ammine complexes in solution has more recently been studied by X-ray absorption fine structure (EXAFS)<sup>5–7</sup> and X-ray diffraction.<sup>8</sup> Alagna *et al.* concluded from the EXAFS experiments that the copper(II) ion was coordinated by five ammonia at equal distances.<sup>5</sup> However, they used a single scattering, plane wave approximation in the data analysis and were not able to resolve the difference in the equatorial and axial distances. Thus, this investigation cannot

be regarded as conclusive evidence for five equal bond lengths as stated by the authors. Sano *et al.* reported a coordination number of about *four* ammonia as determined by EXAFS in a concentrated aqueous solution.<sup>6,7</sup> But at the same time they concluded from the X-ray absorption near-edge structure (XANES) spectrum, contradictory to their EXAFS results, that the geometry is square pyramidal with *five* ammonia coordinated to the copper.

The conclusions from these EXAFS and XANES investigations are not consistent with each other, and they are not consistent with the results from an X-ray diffraction study by Yamaguchi *et al.*<sup>8</sup> Yamaguchi *et al.* reported that four ammonia and two water molecules were bound to copper(II) in an aqueous ammonia solution with the ammonia to copper molar ratio 5:1.<sup>8</sup>

The structure of several different solid copper(II) complexes with ammonia and aliphatic amines has been reported, including coordination of four (square planar)<sup>9,10</sup> and five (square pyramidal with copper lifted above the average nitrogen plane)<sup>11,12</sup> nitrogens and six (distorted square bipyramidal)<sup>13,14</sup> nitrogens.

In this investigation we have used X-ray absorption fine structure (XAFS) spectroscopy to determine the maximum number of coordinated ammonia molecules to copper(II) and the geometry of this complex in liquid ammonia, in which all coordination sites of copper(II) have to be occupied by ammonia molecules. The analysis of the XANES spectra was combined with theoretical calculations by the DV- $X\alpha$  method in order to distinguish between different coordination models.

## Experimental Section

**Sample Preparations.** (Tetraammine)copper(II) nitrate,  $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$ , was prepared by adding a concentrated ammonia solution to a hot aqueous solution of copper(II) nitrate until the formed precipitate dissolved again. The solution was cooled, and the formed crystals were filtered off and dried at  $150\text{ }^{\circ}\text{C}$  for several hours to drive off any excess of ammonia. The sample solutions for XAFS measure-

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- (1) Bjerrum, J.; Ballhausen, C. J.; Klixbüll-Jørgensen, C. *Acta Chem. Scand.* **1954**, *8*, 1275.
- (2) Bjerrum, J. K. *Danske Vidensk. Selsk. Mat.-Fys. Medd.* **1934**, *15* (No. 12).
- (3) Bjerrum, J. K. *Danske Vidensk. Selsk. Mat.-Fys. Medd.* **1932**, *10* (No. 11).
- (4) Rosenblatt, F. Z. *Anorg. Chem.* **1932**, *204*, 351.
- (5) Alagna, L.; Prosperi, T.; Tomlinson, A. A. G.; Vlaic, G. *J. Chem. Soc., Dalton Trans.* **1983**, 645.
- (6) Sano, M.; Maruo, T.; Masuda, Y.; Yamatera, H. *Inorg. Chem.* **1984**, *23*, 4466.
- (7) Sano, M.; Maruo, T.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3287.
- (8) Yamaguchi, T.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 415.

- (9) Emsley, J.; Arif, M. *Inorg. Chim. Acta* **1988**, *154*, 17.
- (10) Emsley, J.; Arif, M. *J. Mol. Struct.* **1990**, *220*, 1.
- (11) Tomlinson, A. A. G.; Hathaway, B. J. *J. Chem. Soc., Ser. A* **1968**, 1905.
- (12) Duggan, M.; Ray, N.; Hathaway, B.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342.
- (13) Elliott, H.; Hathaway, B. J. *Inorg. Chem.* **1966**, *5*, 885.
- (14) Distler, T.; Vaughan, P. A. *Inorg. Chem.* **1967**, *6*, 126.

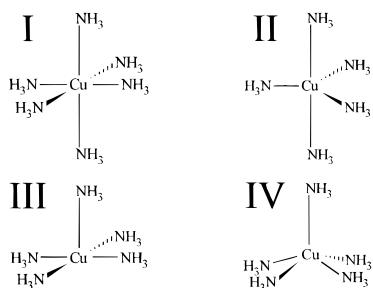


Figure 1. Structural models used in the DV-X $\alpha$  calculations.

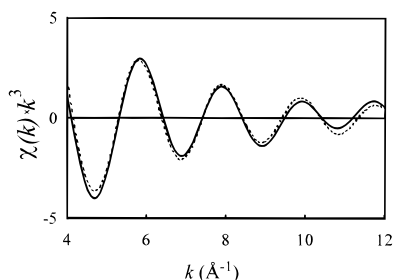


Figure 2. Fourier-filtered experimental (solid line) and fitted (dashed line) EXAFS functions of copper(II) in liquid ammonia.

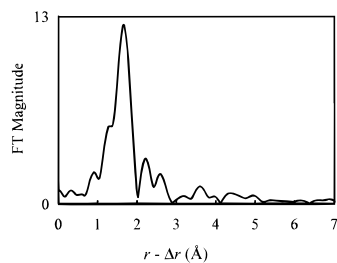


Figure 3. Fourier-transformed EXAFS function (not corrected for phase shift) for copper(II) in liquid ammonia.

ments were prepared in a vacuum system by condensing ammonia on the (tetraammine)copper(II) nitrate powder with a cryostat containing alcohol and dry ice. The copper concentration was 0.4 mol dm<sup>-3</sup>.

**Collection of XAFS Data.** Cu K-edge spectra were collected at the Photon Factory, KEK, Tsukuba, using the unfocused bending magnet beam line 10B under dedicated conditions, 2.5 GeV and 280–350 mA.<sup>15,16</sup> Monochromatic radiation was obtained by using a Si(311) channel-cut monochromator. Two ion chambers with flowing nitrogen and 50% argon in nitrogen for  $I_0$  and  $I$ , respectively, were used for the determination of the radiation intensity in the transmission mode. The energy scale was calibrated by use of the external calibration method, assigning the first inflection point of the Cu K-edge of Cu metal foil to 8 980 eV. The liquid ammonia solutions of copper(II) nitrate was transferred into a high-pressure, stainless steel XAFS cell dipped in a mixture of alcohol and dry ice. The cell with the sample solution was then quickly moved to a vacuum chamber, and the sample was measured at -50 °C by use of a helium-circulated cryostat.

**Processing of EXAFS Data.** The EXAFS data were processed using standard procedures for preedge subtraction, spline fitting and removal, and Fourier transformation.<sup>17</sup> The Fourier filtered data were modeled in the curved wave approximation and refined in  $k$ -space by a least-squares procedure, by use of theoretical amplitude and phase functions as calculated by the computer program FEFF5.<sup>18–20</sup>

**Computations.** The computational details of the DV-X $\alpha$  method

**Table 1.** Results of the EXAFS Curve Fitting for the Copper(II) Ions Solvated in Liquid Ammonia ( $N$ , Coordination Number;  $r$ , Interatomic Distance;  $\Delta E_0$ , Shift in Energy Reference,  $\sigma$ , Debye–Waller Factor;  $\lambda$ , Photoelectron Mean Free Path)

shell	$N^a$	$r/\text{Å}$	$\Delta E_0/\text{eV}$	$\sigma/\text{Å}$	$\lambda/\text{Å}$	$R^c$
1	4	2.00	2.26	0.076	5.41	0.151
2	1	2.19	14.16	0.088	5.94	
1	4	2.00	2.26 <sup>a</sup>	0.080	5.41 <sup>a</sup>	0.145
2	2	2.17	14.16 <sup>a</sup>	0.143	5.94 <sup>a</sup>	
1	4 <sup>b</sup>	2.029 <sup>b</sup>				
2	1 <sup>b</sup>	2.19 <sup>b</sup>				

<sup>a</sup> Value fixed in the final refinement. <sup>b</sup> Crystallographic data from ref 12 included for comparison. <sup>c</sup>  $R = [\sum k^6 \{\chi_{\text{obs}}(k) - \chi_{\text{calc}}(k)\}^2 / \sum k^6 \chi_{\text{obs}}^2(k)]^{1/2}$ .

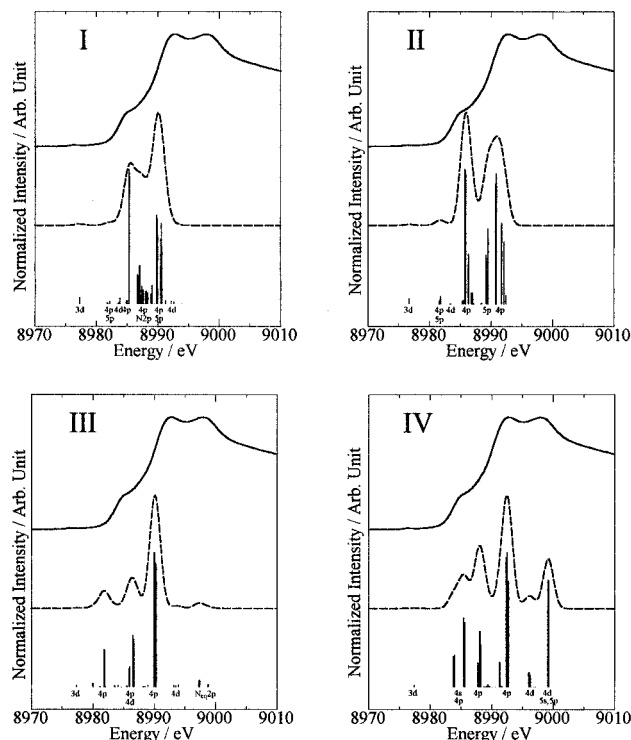


Figure 4. Calculated transitions (vertical bars) and Gaussian-convoluted cross sections (dashed line) for the models I–IV. The experimental XANES (solid line) is given for reference. The vertical bars are labeled with the orbital to which a copper 1s electron is excited. N2p and Neq2p refer to nitrogen orbitals, the others, to copper orbitals.

have previously been described.<sup>21–23</sup> A Slater exchange value,  $\alpha$ , of 0.7 was used. The different models used are shown in Figure 1 and are based on crystal structures reported in the literature,<sup>12,14</sup> which were modified by the results obtained from the EXAFS refinements in this study. The models will hereafter be referred to by their roman numerals, see Figure 1. Model I is based on some (hexaammine)-copper(II) halides,<sup>14</sup> model II on [Cu(tren)(NH<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>,<sup>12</sup> and models III and IV on K[Cu(NH<sub>3</sub>)<sub>5</sub>][PF<sub>6</sub>]<sub>3</sub>.<sup>12</sup> Model III was modified from the crystal structure, model IV, so that the copper(II) ion is placed on the average nitrogen plane. The Cu–N bond lengths were set to 2.00 Å for “equatorial” and 2.19 Å for “axial” bonds. The N–H bond lengths were set to 1.014 Å and the Cu–N–H bond angles to 111.84°.

(18) Mustre de Leon, J.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. B* **1991**, 44, 4146.

(19) Rehr, J. J.; Albers, R. C.; Zabinsky, S. I. *Phys. Rev. Lett.* **1992**, 69, 3397.

(20) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, 113, 5135.

(21) Adachi, H.; Tsukada, M.; Satoko, C. *J. Phys. Soc. Jpn.* **1978**, 45, 875.

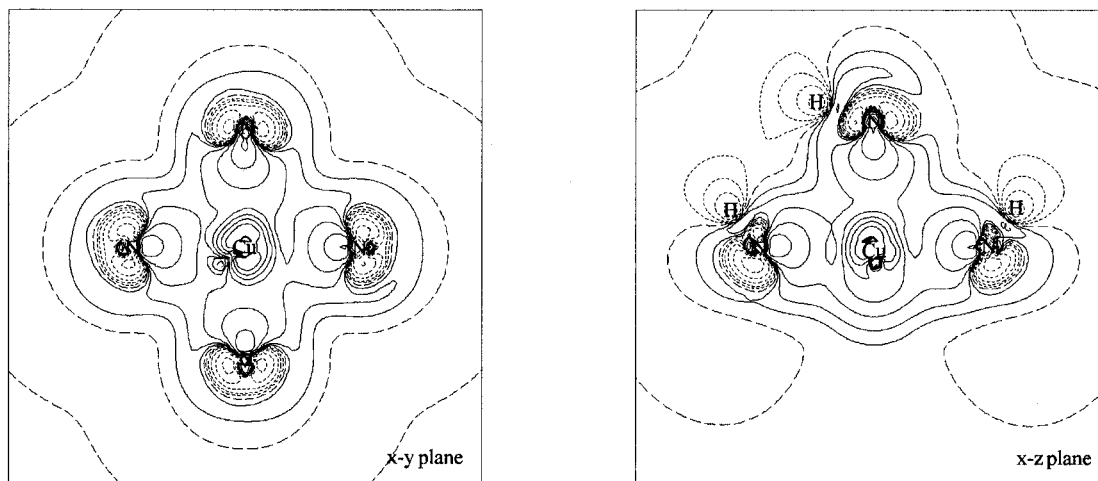
(22) Satoko, C.; Tsukada, M.; Adachi, H. *J. Phys. Soc. Jpn.* **1978**, 45, 1333.

(23) Adachi, H.; Shiokawa, S.; Tsukada, M. *J. Phys. Soc. Jpn.* **1979**, 47, 1528.

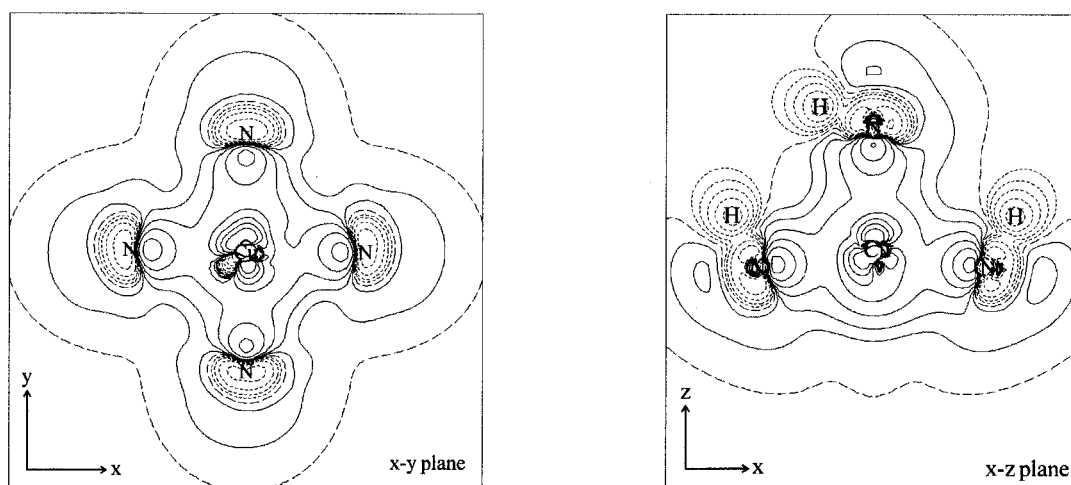
(15) Nomura, M.; Koyama, A. *KEK Report 89-16*; National Laboratory for High Energy Physics: Oho, Tsukuba, Japan, 1989.

(16) Nomura, M.; Koyama, A. In *X-ray Absorption Fine Structure*; Hasnain, S. S., Ed.; Ellis Horwood: London, 1991; p 667.

(17) Sayers, D. E.; Bunker, B. A. In *X-ray Absorption: Principles, Applications, Techniques in XAFS, SEXAFS and XANES*; Koningsberger, D. C., Prins, R., Ed.; John Wiley & Sons: New York, 1988; p 211.



**Figure 5.** Map of change in electron density for model **III** showing the difference in the *xy* and *xz* planes. Solid lines indicate an increased density; long dashed lines, zero change, and short dashed lines, a decreased density.



**Figure 6.** Map of change in electron density for model **IV** showing the difference in the *xy* and *xz* planes. Solid lines indicate an increased density; long dashed lines, zero change, and short dashed lines, a decreased density.

In model **IV** the copper(II) was lifted 0.27 Å above the average nitrogen plane.<sup>12</sup> The ammonia molecules were rotated to an angle giving the highest possible symmetry. Model **III** is thus in  $C_{3h}$  symmetry, and models **I**, **II**, and **IV** are in  $C_s$  symmetry. The basis functions used were the 1s to 5p atomic orbitals for the Cu atom, 1s to 2p for N atoms, and 1s for H atoms. A grid of 10 000 sample points was used in the numerical integration. Self-consistency within 0.005 electrons was obtained for the orbital populations.

## Results

**EXAFS.** The experimental and fitted EXAFS functions are shown in Figure 2, and the corresponding experimental Fourier transform is shown in Figure 3. The best fit was obtained by a two-shell model, with four equal nitrogens in the first shell at a distance of 2.00 Å. However, equally good fits were obtained both with one and two nitrogens at a distance of 2.19 Å in the second shell. Thus, it was not possible to conclude from the EXAFS refinement alone whether there was only one or two nitrogens in the second shell. The results of the curve-fitting are summarized in Table 1.

**Calculations.** Calculated transitions for the four different models and the experimental XANES spectrum are shown in Figure 4. The energy scale was calibrated by assigning the calculated 1s  $\rightarrow$  3d transition to the energy of the preedge peak in the recorded XANES spectrum. Calculated transition energies were convoluted by a Gaussian function with a full-width half-height (FWHH) of 1.0 eV. As can be seen from Figure 4,

models **I–III** all include transitions at energies where none are seen in the experimental XANES spectrum. Only in model **IV** are all the experimentally observed transitions correctly predicted by the DV-X $\alpha$  calculation. Electron density difference for models **III** and **IV** are shown in Figures 5 and 6, respectively.

## Discussion

It has not been possible from the EXAFS analysis alone to conclude whether there is one or two nitrogens in the axial positions of the copper(II) ion. An equally good fit was obtained in both cases; see Table 1. The distances obtained for the complex in solution are, within the error limits of the method, in both cases the same as that for the complex in the solid state.<sup>12</sup> However, a number of parameters had to be fixed in the refinement in order to fit the hexacoordinated model; see Table 1. The average Cu–N distance for the pentacoordinated complex is 2.04 Å. This is the same distance as was found by Alagna *et al.* and which they regarded as evidence for five equal bond lengths.<sup>5</sup> However, they used the plane wave EXAFS approximation in the refinement<sup>5</sup> and were most probably not able to resolve the equatorial and axial distances since the difference is only about 0.2 Å. The equatorial Cu–N distance of 1.93 Å obtained by solution X-ray diffraction<sup>8</sup> seems to be too short, in view of both the present results and earlier results obtained by EXAFS spectroscopy<sup>5–7</sup> and X-ray single crystal

data for similar structures,<sup>11,12</sup> all of which show bond lengths in the range of 2.00–2.05 Å.

The DV–X $\alpha$  calculations clearly show that the octahedral and trigonal bipyramidal models can be discarded. As can be seen from Figure 4, the calculated transition energy patterns do not correspond to transitions observed in the XANES spectrum of the solvated copper(II) ion, and the best agreement between the calculated and experimentally observed transitions is obtained by model **IV**. Thus, it is concluded that the coordination number for copper(II) ions in liquid ammonia is five and that the structure is a square pyramid with the copper lifted above the average nitrogen plane.

A comparison of the electron density difference maps for models **III** and **IV**, Figures 5 and 6, respectively, shows a larger increase in electron density between the copper and nitrogen atoms for model **IV**. This indicates a stronger copper–nitrogen bond and thus a more stable complex. It can also be seen from Figure 5 that there is increasing electron density protruding out from beneath the copper atom (opposite direction to the axial ammonia). This increased electron density would “pull down” the equatorial ammonia ligands, resulting in a model **IV** structure.

Water and ammonia show similar ligand properties, and the hexaaqua copper(II) complex is well-established as having a Jahn–Teller distorted octahedral geometry. Åkesson *et al.* have studied water coordination of first row transition metals in their

di- and trivalent states.<sup>24</sup> They calculated the binding energies  $\Delta E_b^m = E\{M(H_2O)_m^{n+}\} - E\{M^{n+}\} - mE\{H_2O\}$  for penta- ( $m = 5$ ), hexa- ( $m = 6$ ), and heptahydrated ( $m = 7$ ) metals and showed that the ligand field stabilization for copper(II) is largest for the pentahydrate and that the difference in total energy between the penta- and hexahydrate is small.<sup>24</sup> It is thus possible that with a different ligand this order is reversed if the ligand-field stabilization for the pentasolvated ion is large enough. In a more charge-neutralizing solvent than water this difference would be expected to decrease, and it is possible that in a solvent like ammonia the order will be the reversed for the solvated copper(II) ion. Thus, it is not unlikely from a theoretical point of view that pentacoordination should be favored over hexacoordination for copper(II) ammonia complexes.

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(24) Åkesson, R.; Petterson, L. G.; Sandström, M.; Wahlgren, U. *J. Am. Chem. Soc.* **1994**, *116*, 8705.