An Extended X-Ray Absorption Fine Structure Study of Penta-amminecopper(II) Bis(tetrafluoroborate): Evidence for Five Equal Bond Lengths †

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The extended *X*-ray absorption fine structure spectra of powered $[Cu(NH_3)_5][BF_4]_2$ have been measured at room temperature and at 77 K using synchrotron radiation. Standard Fourier-transform and least-squares fitting methods {utilising $[Cu(en)_2][BF_4]_2$ (en = ethylenediamine) as a model complex for extracting amplitude and phase parameters for Cu–N bonds} demonstrate that in each case only a single shell is present about the metal ion, *i.e.* all five Cu–N bonds are of equal length.

The recent crystal-structure determination on $K[Cu(NH_3)_5][PF_6]_3$ has demonstrated that the $[Cu(NH_3)_5]^{2+}$ unit is square-based pyramidal [1] thus filling a lacuna in the large amount of spectroscopic and structural data collected over the years on five-co-ordinate copper(II) complexes with N-donors.[2] A parallel *X*-ray study of aqueous solutions of $[Cu(NH_3)_5(OH_2)]^{2+}$ has, however, led to an estimate of 1.93(2) Å for the in-plane Cu–N bond length.[3] This appears to be anomalously short when compared with values in analogous complexes having axial oxygen rather than nitrogen atoms, but with a roughly similar axial bond length as deduced experimentally for $Cu–N_{ax}$ in this case [3] [*i.e.* 2.3(2) Å]. An example is $[Cu(NH_3)_4(OH_2)]SO_4$,[4] where $Cu–O_{ax}$ 2.34 Å and $Cu–N_{eq}$ 2.03 Å.

This unusual result (which appears to be outside the errors of the solution *X*-ray technique) has prompted us to re-examine the geometry in another member of the penta-ammine series, $[Cu(NH_3)_5][BF_4]_2$, to probe for any further anomalies which might be present. Correlating the e.s.r. spectra, electronic spectra, and unit-cell dimension has long posed a problem.[5] In addition, the absence of reflections at high θ values has precluded study by normal single-crystal *X*-ray methods, so we have utilised extended *X*-ray absorption fine structure (EXAFS) spectroscopy to extract information on bond lengths.

Experimental

The complexes $[Cu(NH_3)_5][BF_4]_2$ and $[Cu(en)_2][BF_4]_2$ (en = ethylenediamine) were prepared by standard methods and characterised by elemental analysis (Found: Cu, 19.6; NH_3, 26.5. Calc. for $H_{15}B_2CuF_8N_5$: Cu, 19.7; NH_3, 26.4. Found: C, 13.5; H, 4.7; N, 15.8. Calc. for $C_4H_{16}B_2CuF_8N_4$: C, 13.45; H, 4.5; N, 15.7%) and electronic spectra.[5] The second of these was chosen as the model complex for comparison of known (*X*-ray determined) distances with those of the penta-ammine because of the equivalent bond lengths (within the error limits of the *X*-ray determination [6]), similar bond type (*i.e.* σ Cu–N), and identical anion. These criteria were chosen to avoid introducing errors in transferring phase shifts.

Samples were finely ground and supported (in as homogeneous a fashion as possible) between Kapton tape. The penta-ammine was also studied at liquid-nitrogen temperature (77 K) maintained throughout the experimental run on a cold-finger of a cryostat with Kapton windows. There was no evidence for decomposition of samples during (colour changes) or after (electronic spectra) recording spectra. The entire *K*-edge and EXAFS regions were recorded over a range of 1 200 eV, starting 160 eV before onset of the edge, at 2-eV intervals. The *K*-edge region alone was also recorded at higher resolution with data points at 0.5-eV intervals, at both temperatures.

Spectra were measured on the *X*-ray spectrometer of the Synchrotron Light Users' Project (PULS) of the Adone Synchrotron, located at Frascati, Italy.[7] A beam current of *ca.* 80 mA was used and the spectra registered in a transmission mode. Standard background subtraction (Victoreen fit), atom-absorption correction, and Fourier-transform analysis were carried out using local programs.[8] The high-energy modulation of the spectra [*i.e.* $\chi(k)$] was extracted using a standard method for subtracting contributions to absorbance due to the absorber alone (*i.e.* Cu) using a Fourier filtration.

Raw spectra are shown in Figure 1, extracted Fourier-filtered EXAFS in Figure 2, and *K*-edge spectra in Figure 3.

Results and Discussion

Data Elaboration.—The moduli of the Fourier transforms of the filtered EXAFS spectra in *R* space are in all three cases dominated by a single well defined peak below 2 Å. All data analysis was concerned with this peak, although we note that $[Cu(en)_2][BF_4]_2$ also showed a clear peak at *ca.* 2.55 Å, due, presumably, to the carbon atoms of the en rings (see Figure 4).

Two methods were used to extract Cu–N bond lengths. First, the inverse transforms of the three cases in *k* space (*k* = photoelectron vector) were explored over various *k* ranges for the major shell. This separates out the contributions to the EXAFS spectra due to this shell alone. For all three cases, there was no evidence for the presence of ' beats ' out to $k = 12$ Å^{-1}.[9] In other words, there were no clear breaks in the real part (*i.e.* the amplitude) of the inverse Fourier transform (see Figure 5) which would indicate differences in bond lengths under the first shell. The Cu–N bond lengths were found by first extracting a phase-shift correction, ΔR_{ij}, from the standard $[Cu(en)_2][BF_4]_2$. This allows for the effect of $\varphi_{ij}(k)$ in the standard, single-scatterer, plane-wave approximation of the EXAFS [equation (1)]. The equation refers to a spherically averaged sample for a 1*s* transition from atom *i* surrounded by N_j atoms at a mean distance R_{ij} having a variant σ_{ij} and which back-scatter with the probability $A_j(k, \pi)$; *k* is the electron wave vector, $\varphi_{ij}(k)$ is the phase shift, and L_{ij} the mean free path determined by inelastic electron-loss mechanisms; μ = absorption coefficient of Cu, μ_0 = free-atom absorption coefficient of Cu.

† *Non-S.I. unit employed*: eV ≈ 1.60×10^{-19} J.

$$\chi(k) = (\mu - \mu_0)/\mu_0 = (1/k)\sum N_j/R_{ij}^2|A_j(k, \pi)|\sin[2kR_{ij} + \varphi_{ij}(k)]\exp(-2k^2\sigma_{ij}^2)\exp[-2R_{ij}/L_{ij}(k)] \quad (1)$$

Plots of R_{ij} *vs.* k were then used further to correct for the k dependence of the bond lengths,[10] *via* equation (2). For these

$$\Delta R_{ij} = (\varphi_{known} - \varphi_{unknown})/2k \quad (2)$$

plots, the maximum k range possible was scanned, neglecting $k \leqslant 3$ Å^{-1}, where single-scatterer theory is known not to apply [11] or {in $[Cu(en)_2][BF_4]_2$} where the signal-to-noise ratio was low because of truncation at $k > 9$ Å^{-1}. The plots were stable and straight in all three cases. The Cu–N distances found for $[Cu(NH_3)_5][BF_4]_2$ are 2.04(1) Å at room temperature (r.t.) and 2.01(1) Å at 77 K. Assuming strict phase-shift transferability, accuracies are generally believed to be ± 0.01 Å.[9,10] The fitting program gives higher apparent accuracies (± 0.005 Å).

The fact that the high-k cut-off is limited (given the low-Z back-scatterer being investigated, *i.e.* N atoms) places a limitation on the resolution in ΔR, given by $n\pi/2k_{max.}$ (n = beat number). Thus, the transform methods above may not have succeeded in defining bond-length differences <0.1 Å. It is then necessary to resort to curve-fitting procedures, using a parametrised version of equation (1) and least-squares methods. Empirical phase parameters were extracted from the back-scattering curve of the major shell for $[Cu(en)_2][BF_4]_2$ (the fixed parameters being, of course, $N = 4$ and $R = 2.25$ Å). These empirical parameters were then inserted into a least-squares fit of the back-transforms of the penta-ammine at both temperatures, this time varying N and R. Attempts to fit $\chi(k)$ to a model having 4 + 1 co-ordination (*i.e.* one Cu–N bond longer than the other four) using literature bond lengths [1] were unsuccessful, as was one with 2 + 2 + 1 co-ordination (see Figure 5 for examples of the quality of fits); nor were fits possible with a 3 + 2 model (*i.e.* three Cu–N bond lengths different from the other two) with a range of bond lengths inputted. A successful fit was possible only for a model having five equal bond lengths. Finally, the poor fit given with five equal bond lengths, but very different from that found, is also shown in Figure 5.

K-*Edge Spectra*.—Although they have been found useful for following oxidation-state changes, the factors responsible

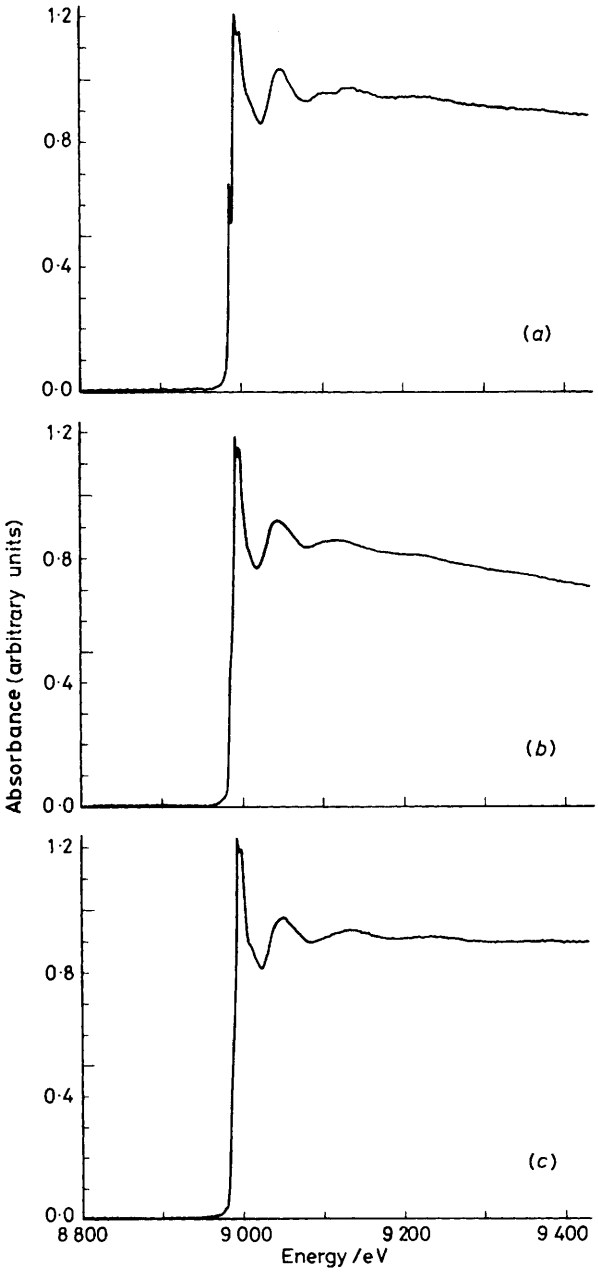

Figure 1. Raw EXAFS spectra of $[Cu(en)_2][BF_4]_2$ (*a*) and $[Cu(NH_3)_5][BF_4]_2$ at r.t. (*b*), and 77 K (*c*)

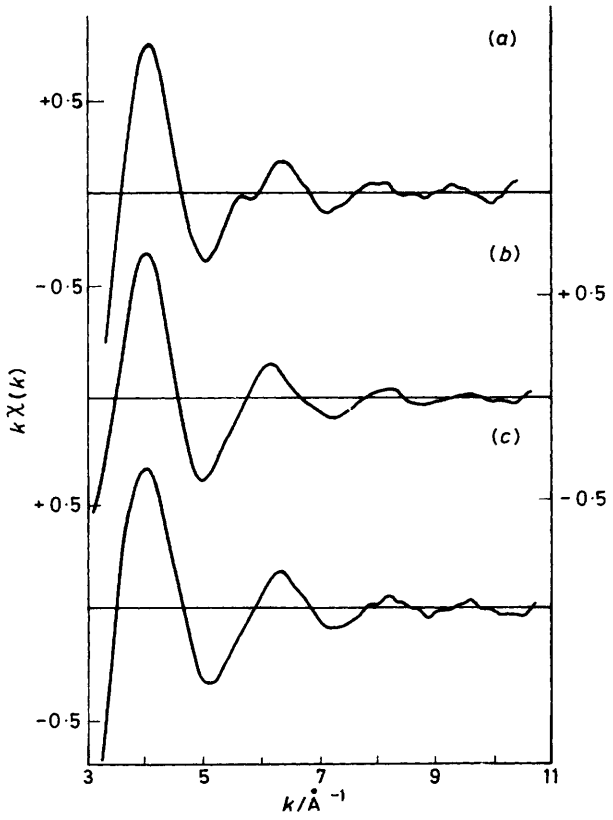

Figure 2. Fourier-filtered EXAFS spectra. Details of complexes as in Figure 1

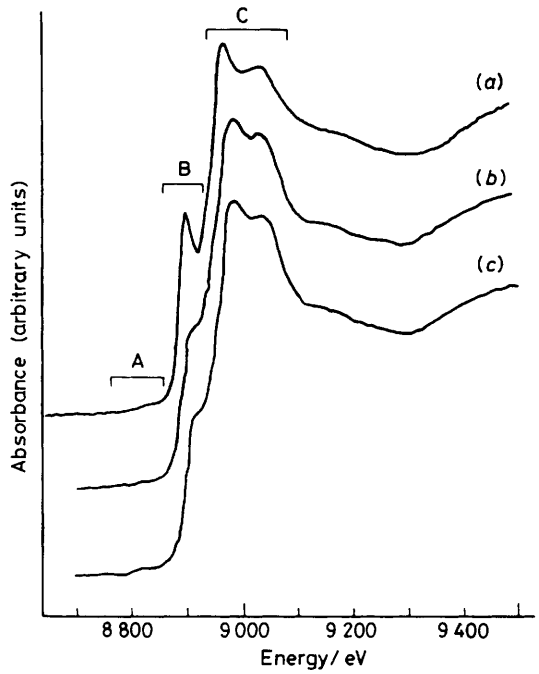

Figure 3. *K*-Edge spectra of the complexes. Details as in Figure 1

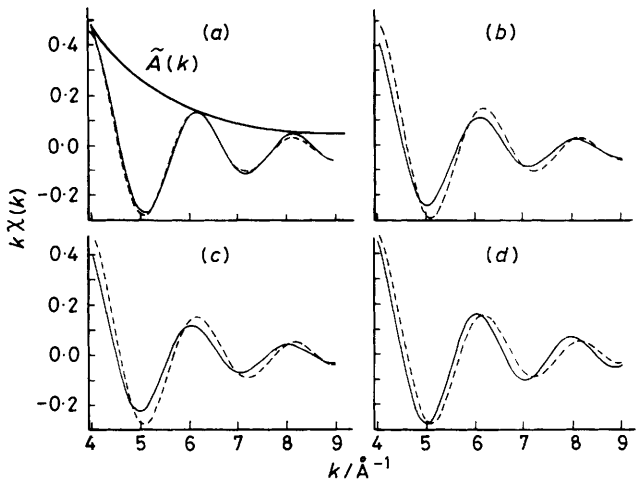

Figure 5. (*a*) ' Best ' fit of the back-transform of the major peak of $[Cu(NH_3)_5][BF_4]_2$ (r.t.), with N_j = 5, all equal: ——, experimental; – – – –, calculated fit. The curve $\tilde{A}(k)$ is the real part (*i.e.* the amplitude) shown to illustrate absence of ' beats.' (*b*)—(*d*) Examples of poor fits: four N atoms at 2.03 Å and one N atom at 2.193 Å; [1] two N atoms at 2.02 Å, two at 2.05 Å, and one at 2.193 Å; and five N atoms at 2.06 Å, respectively. E_0 (the threshold energy) was kept constant in each case, at the first inflection point of the *K*-edge spectrum, throughout the minimisation procedure

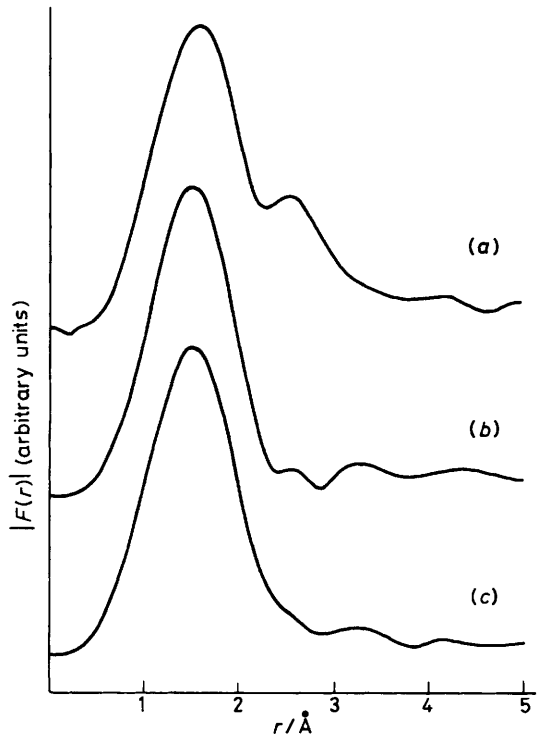

Figure 4. Fourier transforms of the spectra of Figure 2

for energy shifts and intensity changes in *K*-edge spectra (*i.e.* geometry and donor-atom type) are still not clear.[12] All three cases give only very weak absorption in the region usually assigned to the $1s \rightarrow 3d$ transition (' A '),[13] in agreement with an absence of *p*–*d* mixing. Beyond this point, problems arise in assigning spectra. Thus, the *K*-edge spectra of several iron(III) complexes were assigned in region ' B ' as arising from $1s \rightarrow 4s$ transitions (using a $Z + 1$ atomic formalism).[14] However, going from the tetragonal octahedral $[Cu(en)_2][BF_4]_2$ to the five-co-ordinate penta-ammines leads to a decrease in the intensity of this band. Given that a $1s \rightarrow 4s$ transition (which is dipole-forbidden) could acquire intensity only through some mechanism leading to *s*–*p* mixing, the relative intensities for the two complexes would be expected to be in the opposite sense. Similar difficulties have been found with $[Cu(im)_4]^{2+}$ in solution and $[Cu(im)_4][NO_3]_2$ [15] (im = imidazole). In the higher-energy region the peak ' C ' is clearly split into two components in all three cases. Although this presumably indicates that the 4*p* (or *np*-like) orbitals are no longer degenerate, it does not lead to any clear diagnostic capabilities. Indeed, there appears to be little difference in *K*-edge spectra between the room- and low-temperature forms of the penta-ammine despite the clear difference brought to light by the EXAFS results.

Cu–N *Bond Lengths.*—There have been many correlations of axial *vs.* equatorial bond lengths for σ-bonded donor atoms with Cu[II] [16] since the original correlation put forward for the tetra-ammines many years ago.[17] Whenever equal bond lengths have been found they have invariably been in six-co-ordinate complexes in which dynamic Jahn–Teller effects have been identified.[18] To the best of our knowledge, the present case is the first example of equal bond lengths being found in a five-co-ordinate complex. The suspicion then arises that the EXAFS technique, despite all the care taken in analysis using both Fourier-transform and fitting techniques as described above, may not be sufficiently reliable to allow us to come to this conclusion. Thus, errors of up to 0.14 Å have been found for EXAFS-determined Zn–Zn bond lengths when corrections were not made for disorder in the system.[19]

This point may be further probed utilising equation (3).

$$\ln(A_{unknown}/A_{known}) = 2\,\Delta\sigma^2k^2 + 2(R_{known} - R_{unknown})/2kL_{ij} + \ln[(N_{unknown}/N_{known})(R_{known}/R_{unknown})^2] \quad (3)$$

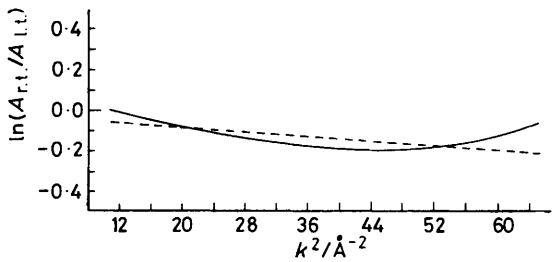

Figure 6. Plot of $\ln(A_{r.t.}/A_{l.t.})$ *vs.* k^2 for $[Cu(NH_3)_5][BF_4]_2$ [see equation (3)]. The ordinate intercept gives the ratio $N_{r.t.}/N_{l.t.}$. The dashed line is the least-mean-squares best-fit straight line. l.t. = Low temperature (77 K)

Plots of the left-hand side of equation (3) *vs.* k^2 should give some indication as to whether truncation at $k \leqslant 3$ Å^{-1} or any amplitude-distortion effects seriously disrupt the analysis. Such a plot for the penta-ammine (Figure 6) at the two temperatures is well behaved and the fact that it is almost a straight line suggests that there are no abnormally large differences in σ on going through the phase change.

On a simplistic basis, the bond length found for the r.t. form would still be in reasonable agreement with the average bond length found (2.06 Å) in the square-based pyramidal $[Cu(NH_3)_5]^{2+}$ unit in $K[Cu(NH_3)_5][PF_6]_3$.[1] We are forced to conclude from this that the close approach of an axial NH_3 combined with lengthening of the in-plane Cu–N distances leads to electronic spectra which are virtually indistinguishable from those of the 'elongated square-based pyramidal' type.[1,2] Unfortunately, the presence of a single shell necessarily means that bond angles cannot be determined using the EXAFS technique (not with the present state of the art, at least), so this must remain as only a tentative conclusion.

Despite this limitation, the bond-length change on going to 77 K is significant and suggests that a significant change in geometry has occurred. From the extensive literature available, a change to (idealised) trigonal-bipyramidal geometry would be expected to give rise to Cu–N bond lengths of *ca.* 2.00—2.02 Å. Thus, Cu–NH_3(axial) 2.023(11) Å in [Cu(tren)$(NH_3)]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine) and 2.00 Å in $[Cu(NH_3)_2][Ag(SCN)_3]$.[20] {The equatorial Cu–NH_3 bond length of 2.05(1) Å in $[Cu(bipy)_2(NH_3)]^{2+}$ (bipy = 2,2′-bipyridyl) may reflect the effect of some steric hindrance from the bulky bipy ligands.[21]} The EXAFS results are in (indirect) agreement with such a change to a more trigonal-bipyramidal geometry. We speculate that the changes are brought about by trapping out of thermal motions of the BF_4^- ion at 77 K, which would cause changes in hydrogen bonding between BF_4^- and ammonia molecules. It is not possible to locate the Cu · · · F and Cu · · · B distances in the transforms with any certainty to provide further evidence on this point.

Acknowledgements

We are deeply indebted to Dr. S. Mobilio, I.N.F.N., and Dr. A. Lapicirella, I.T.S.E., for their help and criticism. We also thank the staff of the Adone Synchrotron for providing beam time and that of the PULS Project for their unfailing help at all times.

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Received 30*th December* 1981; *Paper* 1/1993