Nuclear Quadrupole Resonance Studies (^{63,65}Cu and ^{79,81}Br) of Binuclear Copper(I) Polyhalide Anions

Sundara Ramaprabhu and Edwin A. C. Lucken
Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet, 1211 Genève 4, Switzerland

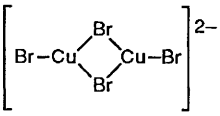
The ^{63,65}NQR spectra of several copper(I) polyhalide anions have been recorded, together with the ^{79,81}Br NQR spectra for the bromides. A Zeeman ^{63}Cu NQR spectrum of a single crystal of $[NPr_4]_2[Cu_2I_4]$ yields the value of 0.262(1) for the asymmetry parameter with the field-gradient z axis perpendicular to the plane of the $[Cu_2I_4]^{2-}$ anion and the x axis along the terminal Cu–I bond. The results are discussed in terms of the electronic structure of these complexes.

The utilisation of nuclear quadrupole resonance (NQR) as a probe for the electronic structure of copper(I) compounds is rendered difficult by the fact that the Cu$^+$ ion has the closed-shell structure $1s^22s^22p^63s^23p^63d^{10}$, with the consequence that the electric field gradients arise from perturbations of this spherically symmetric electron distribution. In terms of the molecular orbitals used by the Cu$^+$ cation the deformation of the spherically symmetric distribution is due both to the creation of a hole in the filled 3d shell and to partial occupation of the hitherto empty 4p orbitals. The field gradients arising from the 3d holes and the 4p electrons are of comparable magnitude but of opposite sign, hence the problems in relating ^{63}Cu coupling constants of copper(I) complexes to their electronic structure. This difficulty is compounded by the fact that the nuclear quadrupole moment of ^{63}Cu is not known with any degree of certainty so that the extraction of field gradients from observed coupling constants is another potential source of error.

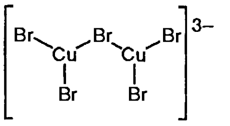
In such circumstances two approaches are possible. One is the semiempirical study of a variety of representative types of complex to provide a background of data which can be used to understand new observations. We have already reported a number of studies of this type.[1,2] The other approach is to carry out molecular orbital calculations on simple compounds of Cu^{I}. The difficulty here is that calculations involving transition metals, even those of the 3d group, are still far from as accurate as those involving atoms of only the first two rows of the Periodic Table. It is therefore essential to have a fairly wide range of simple and, if possible, related compounds whose electronic structures can be calculated using the same method. Bowmaker and co-workers[3,4] have reported such calculations for the diatomic copper(I) halides and the linear copper(I) dihalide anions, **I**, which reveal clearly the difficulties inherent in this problem, for example a strong dependence of the size of the basic 3d and 4p atomic orbitals on the nature of the halogen atom and the degree of co-ordination of the copper atom. In addition to the halide species just mentioned, there exist a number of multinuclear polyhalide anions **II** and **III** whose NQR spectra are unknown. Therefore, in order to provide further data for theoretical calculations of this kind we have measured the ^{63,65}Cu NQR spectra of a number of such species and report the data here, together with ^{79,81}Br NQR data when available.

$[Br{-}Cu{-}Br]^-$

I



II



III

Experimental

All the complexes were prepared according to the published methods.[5–12] In our hands, however, the preparation given for the centrosymmetric $[PPh_4]_2[Cu_2I_4]$ species[12] yielded the non-planar, non-centrosymmetric species and *vice versa*. The unit-cell parameters for the two phases were verified as corresponding to those in ref. 12, and we thank Dr. G. Bernardinelli of this Department for his help in providing these measurements.

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802 digital thermometer and varied between 77 K and room temperature with an Artronix 5301-E temperature controller. Despite numerous attempts, we were unable to observe either ^{63,65}Cu resonance frequencies from $[PBuPh_3]_2[Cu_4Br_6]$ or ^{127}I resonances from any of the iodides at frequencies up to the upper limit of around 65 MHz of our spectrometer. We were also unsuccessful in observing resonances from $[NPr_4]_2[Cu_4Br_6]$ of which a specimen was kindly provided by Professor G. Bowmaker.

A large single crystal of bis(tetrapropylammonium) tetraiododicuprate(I) $[NPr_4]_2[Cu_2I_4]$ was prepared by the slow cooling (20 to 15 °C in 72 h) of a saturated solution in acetonitrile containing a seed crystal suspended from a fine thread. This procedure was repeated several times until the crystal had attained appropriate dimensions (approximately 5 × 5 × 10 mm). Zeeman-split spectra were determined as a function of the orientation of the magnetic field using an assembly of three concentric, mutually perpendicular, Helmholtz coils which were constructed in our work-shops following a published design.[13] We thank Professor A. Weiss for sending us additional constructional details of this device.

Results and Discussion

All four nuclei studied here have spins $I = \frac{3}{2}$ so that the resonance frequencies are related to the coupling constant, e^2Qq_{zz}, and the asymmetry parameter, η, by the relationship (1)

$$\nu = \frac{e^2Qq_{zz}}{2}\left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (1)$$

Table 1 ^{63}Cu NQR frequencies of copper(I) binuclear polyhalides. In all cases the ^{65}Cu frequency was observed at 0.925 times the value of the frequency of the ^{63}Cu isotope

Anion	Cation	ν_{77}/MHz	ν_0/MHz	A/kHz K^{-1}	B/Hz K^{-2}	Structure
$[CuBr_2]^-$	$[PBuPh_3]^+$	28.969	29.236	−3.142	−5.568	5
$[CuBr(Cl)]^-$	$[NBu_4]^+$	29.695	29.868	−1.920	−3.324	6
$[Cu_2Br_4]^{2-}$	$[NEt_4]^+$	30.647	31.133	−5.470	−11.793	7
	$[NMe_3Ph]^+$	32.217	32.574	−4.122	−6.014	8
$[Cu_2Br_5]^{3-}$	$[NMe_4]^+$	31.397	31.680	−3.080	−7.888	9
$[Cu_2I_4]^{2-}$	$[NBu_4]^+$	24.385	24.498	−0.449	−13.381	10
	$[NPr_4]^+$	24.872	25.195	−4.348	−2.233	11
	$[PPh_4]^+$	25.412	25.798	−4.752	−1.956	12
		26.375	26.870	−6.292	−0.321	
	$[PPh_4]^+$	25.293	25.627	−3.692	−6.466	12*

* Centrosymmetric modification.

Table 2 Previously reported NQR frequencies of copper(I) polyhalide anions measured at 77 K or, where denoted by an asterisk, at 298 K

Anion	Cation	Nucleus	Frequency (MHz)	Ref.
$[CuCl_2]^-$	$[NBu_4]^+$	^{63}Cu	30.70	14
		^{35}Cl	9.65	
$[CuCl_2]^-$	$[AsPh_4]^+$	^{63}Cu	31.15	14
		^{35}Cl	9.28*	
		^{35}Cl	9.48*	
$[CuBr_2]^-$	$[NBu_4]^+$	^{63}Cu	28.85	14
		^{79}Br	76.4	
$[CuBr_2]^-$, Br^-	$[PMePh_3]^+$	^{63}Cu	27.47*	15
		^{79}Br	68.90*	
		^{79}Br	72.60*	
$[CuI_3]^{2-}$	$[PMePh_3]^+$	^{63}Cu	26.29*	15
		^{127}I	57.34*	
		^{127}I	61.10*	
		^{127}I	96.74*	
		^{127}I	103.60*	
		^{127}I	108.28*	
$[Cu_4I_6]^{2-}$	$[PMePh_3]^+$	^{63}Cu	26.15	16
		^{63}Cu	26.80	
		^{127}I	35.80	
		^{127}I	36.90	

where the asymmetry parameter is defined as in (2). It is only

$$\eta = (q_{xx} - q_{yy})/q_{zz} \qquad (2)$$

possible to separate the two terms in this equation by means of Zeeman measurements on large single crystals and we have performed such measurements, discussed in more detail below, for $[NPr_4]_2[Cu_2I_4]$ and find the value $\eta = 0.262(1)$. Thus, while it is certain that the asymmetry parameters of the ^{63}Cu nuclei are far from negligible, there is only an error of 4% in identifying the coupling constant with 2ν even when η is as large as 0.5.

^{63}Cu *Resonances.*—The resonance frequencies of the ^{63,65}Cu nuclei, measured at 77 K, are shown in Table 1, while Table 2 shows the results of previous measurements of the NQR frequencies of copper(I) polyhalide anions. In all the complexes other than one of the phases of $[PPh_4]_2[Cu_2I_4]$ where the two copper atoms in the $[Cu_2I_4]^{2-}$ fragments are inequivalent (in this connection the reader's attention is drawn to the Experimental section above) the crystal structure is such that only one type of copper atom is present and all the ^{63,65}Cu NQR results are in accordance with these facts. The temperature dependence was determined in the range 77–300 K and in all cases the resonance frequencies exhibited the normal inverse relationship to temperature with no discontinuities indicative of a phase change. The results were fitted to the quadratic equation (3). The coefficients of this equation are also given in Table 1.

$$\nu_T = \nu_0 + AT + BT^2 \qquad (3)$$

It is now well established that, all other things being equal, the ^{63}Cu resonance frequencies of complex halides of Cu^I are almost always in the order Cl > Br > I. It was thus to be expected that the frequency of the $[CuBr(Cl)]^-$ anion was found to be intermediate between that of $[CuCl_2]^-$ and $[CuBr_2]^-$. This trend is, however, much more marked in the series $[Cu_2X_4]^{2-}$ than in, say, the series $[CuX(dmpy)_2]$ (dmpy = 2,6-dimethylpyridine) where the ^{63}Cu resonance frequencies of the three-co-ordinated copper nuclei are 38.350, 37.614 and 36.694 or 35.300 MHz for X = Cl, Br and I respectively.[1]

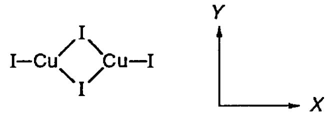
It appears at first sight surprising that the ^{63}Cu resonance frequencies of the three-co-ordinated bromides are slightly higher than those of the two-co-ordinated species, since if the ligands are considered as partial point charges the ratio of the resonance frequencies of the two- to the three-co-ordinate species would be 4:3. However, although the ^{63}Cu resonance frequency of a $[CuI_2]^-$ species is not at present available, this trend might have been guessed at from the frequency of $[CuI_3]^{2-}$.[15] Furthermore, measurements made in this laboratory on the three-co-ordinated copper(I) cations[17,18] show an even greater increase in frequency compared to the analogous two-co-ordinated species.[1] It may therefore be fairly safely assumed that this is a general trend. It may be remarked, moreover, that, in his theoretical studies of bonding in copper(I) halides, Bowmaker[3,4] has observed a marked contraction in the 4p orbitals of Cu^I on going from CuX to $[CuX_2]^-$ so that this evolution may well continue with a further increase of co-ordination number and thus be the origin of the increase in coupling constant.

The resonance frequency of $[NEt_4]_2[Cu_2Br_4]$ is somewhat lower than that of $[NMe_3Ph]_2[Cu_2Br_4]$, probably a reflection of the shorter Cu–Br bond lengths in the latter complex (2.421, 2.417 and 2.310 compared to 2.454, 2.441 and 2.319 Å). It is not so easy to see the same trend in the iodides since the only one of the four species studied which has a notably higher resonance frequency is $[PPh_4]_2[Cu_2I_4]$ in which the anion has lost its centre of symmetry.

The resonance frequency of the $[Cu_2Br_5]^{3-}$ anion is intermediate between that of the two $[Cu_2Br_4]^{2-}$ species. This seems to be again reflected in the Cu–Br bond lengths, for while the opening of one of the halogen bridges results in an evening out of the lengths of the three Cu–Br bonds (2.392, 2.397 and 2.381 Å) the average Cu–Br bond length (2.390 Å) is intermediate between those of the two $[Cu_2Br_4]^{2-}$ anions (2.405 and 2.383 Å).

Zeeman Study of ^{63}Cu *in* $[NPr_4]_2[Cu_2I_4]$.—The zero-splitting locus method[19] for the determination of the asymmetry parameter was chosen in view of the fact that the resonance line (23.780 MHz at 298 K) was not particularly intense. The salt $[NPr_4]_2[Cu_2I_4]$ crystallises in the monoclinic space group $P2_1/n$ [$a = 9.017(3)$, $b = 12.683(3)$, $c = 16.140(5)$

Å and β = 93.15(3)°]. The loci were obtained in a laboratory system of axes in which the *Y* axis coincided with the crystal *a* axis. This choice was essentially dictated by the need to maximise the signal intensity by placing the axis of the radio frequency coil, which lay along the *Z* axis, roughly perpendicular to the field-gradient *z* axes of both sites. The results were subsequently transformed to the orthogonal ABC reference frame (A and B parallel to the *a* and *b* crystal axes, C perpendicular to the *ab* plane) which reflects the symmetry relationship between the two sites.



In agreement with the crystal structure two distinct loci were observed (Fig. 1), the axis of the elliptical cone formed by the zero-splitting vectors defining the field-gradient *z* axis while the major and minor axes of the ellipse lie along the *y* and *x* axes respectively. The direction cosines of the principal values of the two field-gradient tensors are shown in Table 3 together with those of the molecular vectors defined below. They show that, within experimental error, the field-gradient *z* axis lies perpendicular to the $[Cu_2I_4]^{2-}$ plane while the field-gradient *x* axis lies along the terminal Cu–I bond. The asymmetry parameter has the value 0.262(1). This is similar to those for the three-co-ordinated halogen-bridged triphenylphosphine complexes[20] shown below, but, whereas in all cases the *z* axis is perpendicular to the $PCuX^1X^2$ plane, it is the *y* axis which lies along the terminal Cu–P bond. Finally, in the monomeric complex $[CuBr(PPh_3)_2]$ the *z* axis is perpendicular to the P^1P^2CuBr plane while the *x* axis lies along the Cu–Br bond.[21]

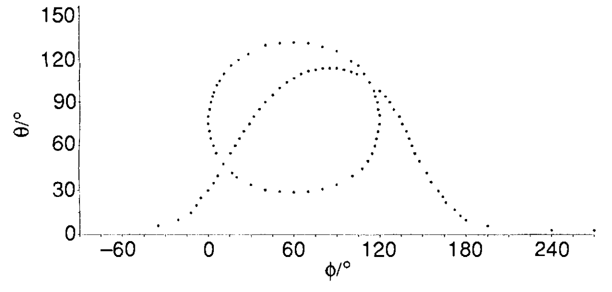
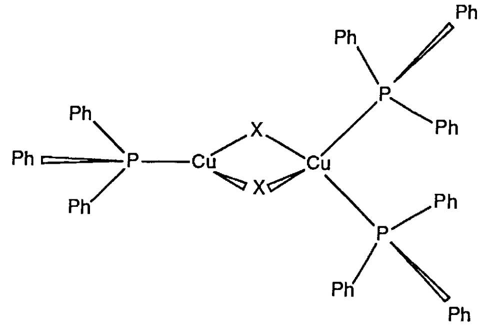


Fig. 1 ^{63}Cu NQR Zeeman zero-splitting loci for $[NPr_4]_2[Cu_2I_4]$

Table 3 The direction cosines of the field-gradient axes for $[NPr_4]_2$-$[Cu_2I_4]$ in the ABC reference frame. Also shown are the direction cosines of the vectors X_m (along the terminal Cu–I bonds), Y_m (the vector lying in the planes of the $[Cu_2I_4]^{2-}$ anions and perpendicular to X_m) and Z_m (the vector perpendicular to the plane of the $[Cu_2I_4]^{2-}$ anions). The asymmetry parameter is 0.262(1) and the angle between the two q_{zz} directions is 34.0° (32.3° between the two vectors perpendicular to the planes of the two $[Cu_2I_4]^{2-}$ anions)

	Axis		
	l	*m*	*n*
q_{xx}	0.105	±0.771	−0.628
X_m	0.083	±0.773	−0.630
q_{yy}	−0.535	±0.546	0.645
Y_m	−0.531	±0.569	0.628
q_{zz}	0.866	±0.292	0.405
Z_m	0.843	±0.278	0.460



^{79,81}Br *Resonances*.—In view of the absence of phase changes, the temperature dependence of the ^{79,81}Br frequencies was observed through just two measurements, at 77 K and at room temperature. The signals were, however, weak and some of the resonances could not be observed at both temperatures. The observed frequencies have been attributed to either ^{79}Br or ^{81}Br on the basis of the known ratio (1.1970:1) of the respective quadrupole moments, combined, where necessary, with the fact that the sensitivity of our spectrometer leaves much to be desired above 65 MHz. The results are shown in Table 4.

The crystal structure of the two $[Cu_2Br_4]^{2-}$ anions indicates that there should be just two distinct ^{79}Br frequencies, one arising from the terminal and the other from the bridging halogen nuclei. Both frequencies were observed only for the $[NEt_4]_2[Cu_2Br_4]$ species, and even for this the lower frequencies could not be found at 77 K. For $[NEt_4]_2[Cu_2Br_4]$ both frequencies are noticeably lower than those of the $[CuBr_2]^-$ anion, presumably since the appetite of the central copper atom for electrons is now satisfied by three ligands. In a molecule containing both terminal and bridging halogen atoms, if the metal–halogen bonds are both of essentially similar types, for example if both are σ bonds, then it is to be expected[22,23] that the bridging halogens would have markedly lower resonance frequencies. This situation seems to prevail for complexes of non-transition metals. If there is a major difference in the nature of the bonds to the terminal and to the bridging halogens, for example if the π character of the terminal bonds is very different from that of the bridging bonds, then this trend may be reversed, and arises for bridged complexes of transition metals.[23] A definitive attribution must, however, await the measurement of Zeeman-split spectra, but we have not, so far,

Table 4 ^{79,81}Br NQR frequencies of copper(I) binuclear polyhalides, with approximate signal-to-noise ratios in parentheses

		Frequency (MHz)			
		77 K		298K	
Anion	Cation	^{79}Br	^{81}Br	^{79}Br	^{81}Br
$[Cu_2Br_4]^{2-}$	$[NEt_4]^+$			45.406(3)	37.940(8)
		64.733(7)	54.071(9)	62.377(5)	52.115(10)
	$[NMe_3Ph]^+$	50.291(4)	42.013(4)	48.222(3)	40.313(3)
$[Cu_2Br_5]^{3-}$	$[NMe_4]^+$	55.776(8)	46.603(11)	54.204(8)	45.311(7)
		57.697(8)	48.208(12)	55.654(8)	46.487(8)
					60.440(4)

been successful in growing sufficiently large crystals for this purpose.

The ^{79,81}Br frequencies of $[Cu_2Br_5]^{3-}$, however, support the attribution of the lower frequencies to the terminal atoms. The crystal structure reveals that there are three distinct sites for the bromine atoms, one bridging and two terminal, and there are indeed three distinct resonance frequencies. Since two of them are noticeably lower than the other the only reasonable assumption is that the highest frequency is that of the bridging halogen since the crystallographic data indicate no very marked difference between the two terminal Cu–Br bonds. Once again a definitive attribution of the resonance frequencies must await a Zeeman study.

Acknowledgements

We thank the Swiss National Research Fund for their support and Dr. Li Pang for his help with the Zeeman study.

References

1 A. Habiyakare and E. A. C. Lucken, *J. Mol. Struct.*, 1989, **213**, 231.
2 A. Habiyakare and E. A. C. Lucken, *Z. Naturforsch., Teil A*, 1990, **45**, 224.
3 G. A. Bowmaker and P. D. W. Boyd, *J. Mol. Struct.*, 1985, **122**, 299.
4 G. A. Bowmaker, P. D. W. Boyd and R. J. Sorrenson, *J. Chem. Soc., Faraday Trans. 2*, 1985, 1023.
5 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1986, **40**, 210.
6 M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1984, **38**, 57.
7 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 135.
8 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1985, **39**, 423.
9 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1985, **39**, 47.
10 M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 751.
11 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 411.
12 H. Hartl, I. Brüdgam and F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, 1985, **40**, 1032.
13 V. Nagarajan, N. Weiden, R. Wendel and A. Weiss, *J. Magn. Reson.*, 1982, **47**, 28.
14 G. A. Bowmaker, L. D. Brockliss and R. Whiting, *Aust. J. Chem.*, 1973, **26**, 29.
15 G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37.
16 G. A. Bowmaker, L. D. Brockliss, C. D. Earp and R. Whiting, *Aust. J. Chem.*, 1973, **26**, 2593.
17 A. Habiyakare and E. A. C. Lucken, to be published.
18 A. Habiyakare, Thesis, Université de Genève, 1990.
19 T. P. Das and E. L. Hahn, *Nuclear Quadrupole Resonance Spectroscopy*, Academic Press, New York, 1958.
20 H. Negita, M. Hiura and T. Okuda, *J. Mol. Struct.*, 1980, **58**, 205.
21 T. Okuda, M. Hiura and H. Negita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1920.
22 E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York, 1969.
23 Yu. A. Buslaev, E. A. Kravchenko and L. Kolditz, *Coord. Chem. Rev.*, 1987, **82**, 7.

Received 22*nd March* 1991; *Paper* 1/01389K