Copper-63,65 Nuclear Quadrupole Resonance Studies of Copper(I) Complexes with Sulfur-containing Ligands. Part 2.[1] Bis(1-Alkylimidazolidine-2-thione)copper(I) Iodides and Related Compounds *

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The ^{63}Cu NQR resonances frequencies of ten three-co-ordinated copper(I) complexes, in each of which at least two of the ligands are thiones, have been determined. The Zeeman splitting of the ^{63}Cu NQR spectrum of a single crystal of bis(tetrahydro-1*H*-pyrimidine-2-thione)copper(I) chloride yields the value of 0.36(2) for the asymmetry parameter with the field-gradient *z* axis perpendicular to the CuS_2Cl plane and the *y* axis along the Cu–Cl bond. The crystal structure of a representative member of these complexes, bis(1-propylimidazolidine-2-thione)copper(I) iodide, confirms the three-co-ordination of the Cu^I. When one of the ligands is a halogen atom the results confirm the previously reported trend that, for a given ligand, the ^{63}Cu NQR resonance frequencies of the complexes $[CuL_2X]$ are in the order Cl > Br > I. For two of the complexes the temperature dependence of the NQR frequency indicates that a phase change occurs in the range 77–300 K.

We have previously reported [1] a study of the ^{63}Cu NQR spectra of various three-co-ordinated complex copper(I) chlorides and bromides with sulfur-containing ligands. That study allowed us to compare the complexing behaviour of these ligands towards copper(I) with that of substituted pyridines[2,3] and of triphenylphosphine.[4,5] In completion of this study we report here the results for a series of bis(*N*-alkylimidazolidine-2-thione)copper(I) iodides and several related complexes: $[CuL_2I]$ [L = 1-methylimidazolidine-2-thione **1**, 1-ethylimidazolidine-2-thione **2**, 1-propylimidazolidine-2-thione **3**, 1-isopropylimidazolidine-2-thione **4** or hexahydro-2*H*-azepine-2-thione (thiocaprolactam) **5**], $[CuL_3]NO_3$ **6** [L = 1-methylimidazoline-2(3*H*)-thione], $[Cu_2L_6(SO_4)]$ (L = 1,3-thiazolidine-2-thione **7** or imidazolidine-2-thione **8**), $[Cu_2L_5(SO_4)]\cdot 3H_2O$ **9** [L = 1-methylimidazoline-2(3*H*)-thione] and $[CuL_2Cl]$ **10** [L = tetrahydro-1*H*-pyrimidine-2-thione]. A complete interpretation of the results of the previous study was not possible owing to the fact that the NQR frequencies of nuclei with spin $\frac{3}{2}$ such as ^{63}Cu depend both on the coupling constant and on the asymmetry parameter. We have therefore observed the Zeeman splitting of the NQR spectrum of a single crystal of a typical member of this series **10**, and thus obtained the separate values of the coupling constant and the asymmetry parameter as well as the directions of the principal values of the field-gradient axes in the molecular framework. Finally, in order to extend our knowledge of the crystal structures of these complexes and to be sure that the iodides are similar to the chlorides and bromides, we have also determined the crystal structure of **3**.

Experimental

Preparations.—The *N*-alkylimidazolidine-2-thiones were prepared according to a published procedure[6] while the remaining ligands are commercially available (Aldrich, Fluka). The complexes **5**–**9** were prepared according to published procedures.[7–11] The four previously unreported bis(*N*-alkylimidazolidine-2-thione)copper(I) iodides, **1**–**4**, were prepared according to the method in ref. 11. All four complexes gave satisfactory C, H and N analyses, carried out by Dr. H. Eder of the University Microanalytical Laboratory. Complex **10** was prepared according to the method in ref. 12 and a large single crystal was prepared by slow cooling, from 15 to 10 °C in 72 h, of a saturated aqueous solution of the complex in which a seed crystals was suspended. This process was repeated several times until the crystal had attained the approximate dimensions 10 × 10 × 7 mm.

NQR Spectroscopy.—The 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. Zeeman-split spectra of a single crystal of complex **10** were observed as a function of the orientation of the magnetic field using the previously reported assembly of three concentric, mutually perpendicular, Helmholtz coils.[13] The crystal was oriented so that its *c*,*b*,*a* axes were aligned along the laboratory *X*,*Y*,*Z* reference frame.

X-Ray Crystallography.—Pale yellow crystals of complex **3** were grown at room temperature from MeOH–MeCN solution. The crystals are elongated thin plates and most exhibit a twin plane perpendicular to the small growing direction [010]. An untwinned thin crystal (0.05 × 0.22 × 0.35 mm) was sealed in a Lindemann capillary under argon to prevent degradation. Cell parameters and intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Two reference reflections were monitored every 60 min and showed a decrease

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Summary of crystal data, intensity measurement and structure refinement for complex **3**

Formula	$C_{12}H_{24}CuIN_4S_2$
M	478.9
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.412(2)
b/Å	16.452(3)
c/Å	15.443(4)
β/°	90.42(1)
U/Å^3	1883.2(8)
Z	4
$F(000)$	952
D_c/g cm^{-3}	1.69
μ(Mo-Kα)/mm^{-1}	3.069
Minimum, maximum A*	1.165, 1.878
$[(\sin\theta/\lambda]_{max}$/Å^{-1}	0.58
T/K	298
No. measured reflections	3085
No. observed reflections	1757 $[\lvert F_o\rvert > 4\sigma(F_o)]$
No. parameters	199
Weighting scheme	$w = 1$
Maximum, average Δ/σ	0.036, 0.004
Maximum, minimum Δρ/e Å^{-3}	0.97, −1.08
S	2.90
R, R'	0.053, 0.053

Table 2 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for **3**

Atom	X/a	Y/b	Z/c
I	0.227 8(2)	0.861 29(6)	0.340 42(6)
Cu	0.216 7(2)	0.707 7(1)	0.332 51(9)
S(1)	0.219 3(5)	0.640 4(2)	0.207 4(2)
N(1)	0.204(2)	0.785 6(8)	0.126 5(6)
N(2)	0.228(2)	0.684 9(7)	0.041 2(6)
C(1)	0.218(2)	0.706 3(9)	0.122 1(7)
C(2)	0.209(2)	0.823 9(8)	0.043 0(8)
C(3)	0.225(2)	0.753 9(8)	−0.017 7(7)
C(4)	0.300(4)	0.606(2)	0.013(1)
C(41)	0.162(6)	0.601(2)	0.007(3)
C(5)	0.174(5)	0.572(2)	−0.063(2)
C(51)	0.290(6)	0.580(2)	−0.056(3)
C(6)	0.252(2)	0.492(1)	−0.090 1(9)
S(01)	0.206 4(6)	0.622 5(2)	0.445 5(2)
N(01)	0.230(2)	0.753 7(7)	0.547 8(6)
N(02)	0.190(2)	0.642 6(7)	0.616 9(6)
C(01)	0.211(2)	0.674 4(8)	0.540 1(7)
C(02)	0.218(2)	0.781 6(8)	0.638 6(8)
C(03)	0.209(2)	0.701 5(9)	0.687 5(7)
C(04)	0.159(2)	0.553(1)	0.636 9(9)
C(05)	0.332(2)	0.512(1)	0.652(1)
C(06)	0.288(3)	0.422(1)	0.673(1)

in intensities of about 8% during the data collection. All reflections were corrected for this drift. Data were corrected by Lorentz polarization and for absorption.[14] The structure was solved by direct methods[15] and refined by least squares with the XTAL program.[16] Atomic scattering factors and anomalous dispersion terms were taken from ref. 17. All hydrogen atom coordinates were calculated. The propyl substituent of one of the imidazolidines shows a crossed disorder of the two ethylenic carbon atoms. This was correctly solved by splitting the two atomic sites involved.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

X-Ray Crystallography.—A summary of the crystal data, intensity measurements and structure refinements is given in Table 1. The atomic coordinates are reported in Table 2, selected geometrical parameters in Table 3. The general conformation of the molecule, Fig. 1, is quasi-planar (average and maximum deviations of the mean plane calculated through all atoms, except the propyl substituents, 0.052 and 0.165 Å respectively). The dihedral angles between the coordination plane and the imidazolidine mean planes are 5.7(4) and 4.5(4)° respectively. The copper lies in an essentially trigonal-planar environment [distance from Cu to plane of the three co-ordinated atoms = 0.008(2) Å]. Although the sum of the bond angles around the copper is 360°, the opening of the I–Cu–S angles is correlated to a repulsive interaction between the iodine atom and the hydrogen of the non-substituted nitrogen of the imidazolidine rings {I ··· H[N(1)] 2.48, I ··· H[N(01)] 2.61 Å}. Consequently, the S–Cu–S bond angle decreases significantly to a value of 111.4(1)°.

An analysis of the molecular packing shows that the molecular planes are nearly parallel to the *bc* plane with the Cu–I bond almost parallel to the *b* axis (Fig. 2). Both imidazolidine rings participate in stacking interactions with equivalent molecules related by the glide plane perpendicular to the *b* axis (angle between the mean planes of the involved

Table 3 Bond lengths (Å) and selected bond angles and torsional angles (°) for complex **3**

I–Cu	2.531(2)	C(41)–C(51)	1.41(6)
Cu–S(1)	2.227(4)	C(5)–C(6)	1.50(4)
Cu–S(01)	2.240(4)	C(51)–C(6)	1.55(4)
S(1)–C(1)	1.71(1)	S(01)–C(01)	1.69(1)
N(1)–C(1)	1.31(2)	N(01)–C(01)	1.32(2)
N(1)–C(2)	1.44(2)	N(01)–C(02)	1.48(2)
N(2)–C(1)	1.30(1)	N(02)–C(01)	1.31(1)
N(2)–C(3)	1.45(2)	N(02)–C(03)	1.46(2)
N(2)–C(4)	1.46(3)	N(02)–C(04)	1.52(2)
N(2)–C(41)	1.56(4)	C(02)–C(03)	1.52(2)
C(2)–C(3)	1.49(2)	C(04)–C(05)	1.47(2)
C(4)–C(5)	1.59(4)	C(05)–C(06)	1.55(2)
I–Cu–S(1)	122.5(1)	I–Cu–S(01)	126.0(1)
Cu–S(1)–C(1)	110.7(5)	Cu–S(01)–C(01)	110.9(5)
C(1)–N(1)–C(2)	113(1)	C(01)–N(01)–C(02)	113(1)
C(1)–N(2)–C(3)	113(1)	C(01)–N(02)–C(03)	114(1)
S(1)–C(1)–N(1)	126.3(9)	S(01)–C(01)–N(01)	125.4(9)
S(1)–C(1)–N(2)	125(1)	S(01)–C(01)–N(02)	125(1)
N(1)–C(1)–N(2)	109(1)	N(01)–C(01)–N(02)	109(1)
N(1)–C(2)–C(3)	103(1)	N(01)–C(02)–C(03)	102(1)
N(2)–C(3)–C(2)	102.2(9)	N(02)–C(03)–C(02)	102.0(9)
S(1)–Cu–S(01)	111.4(1)		
I–Cu–S(1)–C(1)	−3.0(5)	I–Cu–S(01)–C(01)	−1.2(5)
S(01)–Cu–S(1)–C(1)	177.6(4)	S(1)–Cu–S(01)–C(01)	178.2(5)
Cu–S(1)–C(1)–N(1)	−5(1)	Cu–S(01)–C(01)–N(01)	−4(1)
Cu–S(1)–C(1)–N(2)	176(1)	Cu–S(01)–C(01)–N(02)	173(1)

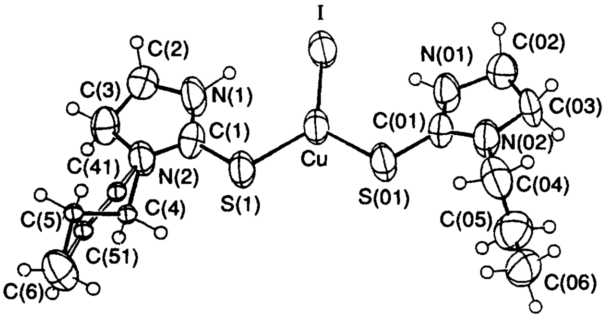

Fig. 1 An ORTEP[18] view of complex **3** with atom numbering. Ellipsoids are represented with 50% probability and disordered atoms [C(4), C(41), C(5) and C(51)] with an arbitrarily fixed atomic radius

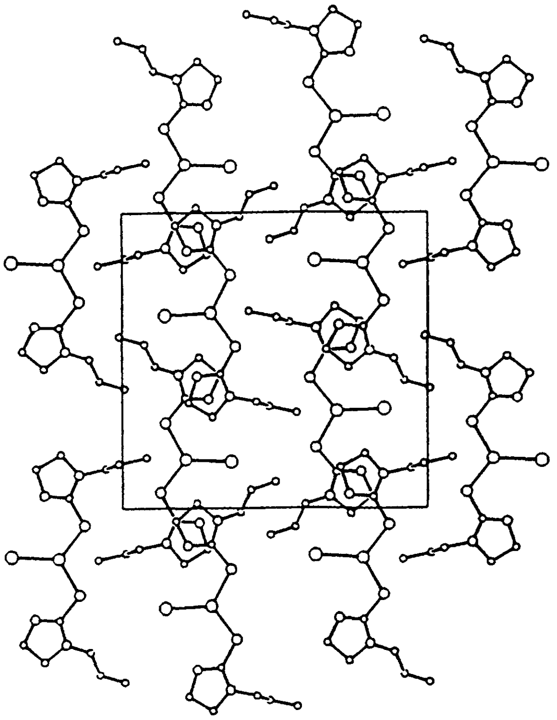

Fig. 2 Projection of the structure along the *a* axis showing the stacking interactions between the imidazolidine moieties

Table 4 Copper-63 NQR frequencies and their temperature dependence. In all cases ^{65}Cu resonances were observed at a frequency of 0.925 times that of the ^{63}Cu resonance

Complex	ν_{77}/ MHz	ν_0/ MHz	A/kHz K^{-1}	B/Hz K^{-2}
1	28.150	28.490[a]	−4.118	−9.176
		28.186[b]	−1.870	−4.918
2	27.948	28.393	−5.803	0.072
3	27.462	27.163	−1.841	−11.443
4	28.591	29.097	−6.343	−2.410
5	29.486[c]	29.777[c]	−3.284	−5.314
	28.480	28.780[c]	−3.397	−4.654
		30.136[d]	−6.142	0.391
6	32.549	33.137	−6.570	−9.430
7	31.773[e]			
	31.734[e]			
8	32.607	32.815	−2.366	−5.850
9	27.926	28.221	−3.417	−3.392
	27.285	27.439	−1.380	−6.861

[a] For the phase in the temperature range 77–113 K. [b] For the phase in the range 114–300 K. [c] For the phase in the range 77–206 K. [d] For the phase in the range 207–306 K. [e] At 300 K.

Table 5 Direction cosines of the components of the field-gradient tensor and of the molecular vectors *x*,*y*,*z* defined in Fig. 4, with respect to the directions of the *a*,*b*,*c* axes of the crystal

Vector	l	m	n
q_{xx}	0.725(8)	±0.663(4)	±0.187(15)
q_{yy}	0.674(14)	±0.739(11)	±0.013(6)
q_{zz}	0.141(12)	±0.119(15)	±0.983(5)
x	0.6961	±0.6961	±0.1752
y	0.7071	±0.7071	0.0000
z	0.1239	±0.1239	±0.9845

imidazolidines = 2.2 and 2.0°, average interatomic distances = 3.62 and 3.73 Å).

NQR Spectroscopy.—The resonance frequencies of the com-plexes are shown in Table 4. The temperature dependence of the resonance frequencies was observed in the range 77–300 K and the results fitted to the quadratic equation (1). The coefficients

$$\nu_T = \nu_0 + AT + BT^2 \qquad (1)$$

of this equation are in Table 4. Both ^{63}Cu and ^{65}Cu have $I = \frac{3}{2}$ so that the resonance frequencies are related to the coupling constant, e^2Qq_{zz}, and the asymmetry parameter, η, by equation (2) where the asymmetry parameter lies between the limits

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

$0 \leqslant \eta \leqslant 1$ and is defined as $(q_{xx} - q_{yy})/q_{zz}$. Even for appreciable values of the asymmetry parameter the coupling constant is approximately twice the resonance frequency; thus for $\eta = 0.3$ there is only a 1.5% difference between 2ν and the exact coupling constant. It is, however, only possible to determine the value of η by Zeeman measurements on large (≈ 1 cm^3) single crystals. Such a measurement was performed for complex **10** the crystal structure of which[19] is very similar to those of **3** and **5**. The measurements were performed using the zero-splitting locus method,[20] the resonance frequency at 289 K being 29.691 MHz. In accordance with the crystal structure,[19] four distinct zero-splitting loci were observed, Fig. 3, leading to a value of 0.36(2) for the asymmetry parameter and hence a coupling constant of 58.1 MHz. The direction cosines of the principal values of the field-gradient tensors are shown in Table 5, together with the direction cosines of the vectors *x*, *y* and *z* shown in Fig. 4. They show that, within experimental error, the field-gradient *z* axis lies perpendicular to the CuS_2Cl plane while the field-gradient *y* axis lies along the Cu–Cl bond.

There is no simple way to interpret the quadrupole coupling tensor of a copper(I) ion. The difficulty springs from the fact that

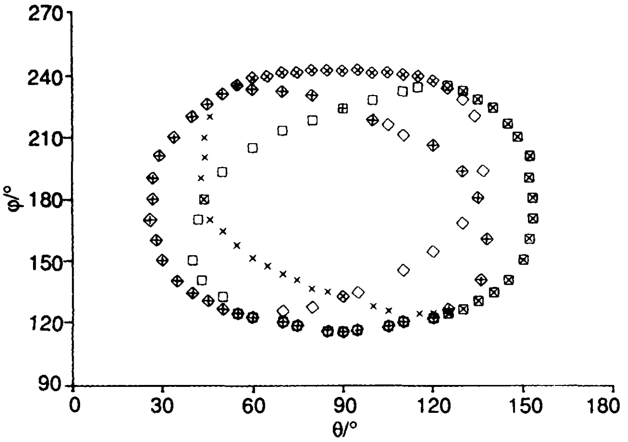

Fig. 3 Zero-splitting loci of the ^{63}Cu NQR Zeeman spectrum of complex **10**

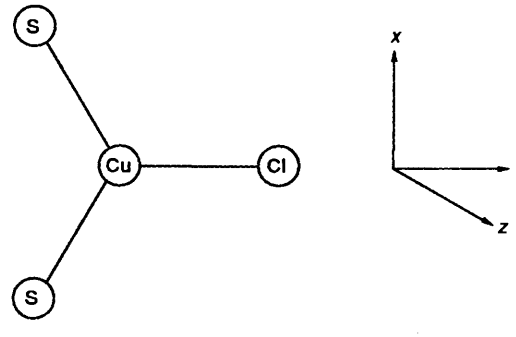

Fig. 4 The directions of the field-gradient principal axes in complex **10**

while the 3d shell is completely filled, and therefore does not formally contribute to the field gradient, it is also highly polarizable. The 3d electrons must therefore either be included in the bonding scheme, in which case the result will be the creation of a hole in the 3d shell, or their polarizability must be taken into account after the construction of a set of 4s–4p molecular orbitals through some sort of Sternheimer shielding effect. An alternative approach which avoids the difficulties of constructing formal bonding schemes but concentrates instead on relating the quadrupole coupling to the nature of the ligands and to the precise way in which they are disposed around the metal atom is the use of partial field gradients. As we shall now see, these two approaches do not however lead to similar conclusions.

The compounds discussed here are all planar three-co-ordinated complexes of the general formula $CuL^a{}_2L^b$ having C_{2v} symmetry. If, for the moment, contributions from the 3d shell are neglected then one may construct appropriately hybridized acceptor orbitals using the vacant 4s and 4p orbitals [equations (3)–(6)]. The axes are chosen such that the z axis is

$$\varphi_z = 4p_z \tag{3}$$

$$\varphi^{a1} = \frac{1}{\sqrt{2}}[(1 - \cot^2\gamma)^{\frac{1}{2}}\cdot 4s - (\cot\gamma)\cdot 4p_x + p_y] \tag{4}$$

$$\varphi^{a2} = \frac{1}{\sqrt{2}}[(1 - \cot^2\gamma)^{\frac{1}{2}}\cdot 4s - (\cot\gamma)\cdot 4p_x - p_y] \tag{5}$$

$$\varphi^{b} = (\cot\gamma)\cdot 4s - (1 - \cot^2\gamma)^{\frac{1}{2}}\cdot 4p_x \tag{6}$$

perpendicular to the plane, and the x axis lies along the unique CuL^b bond. The L^{a1}–Cu–L^{a2} angle is 2γ. If the populations of these orbitals are, respectively, n, a, a and b (the C_{2v} symmetry of the molecule requires that the populations of φ_{a1} and φ_{a2} be identical) and if e^2Qq_o is the atomic coupling constant for the ^{63}Cu nucleus, we may derive expressions (7) and (8) relating

$$n - b = \frac{e^2Qq_{zz}}{e^2Qq_o}\left(1 + \frac{\eta}{3}\right) \tag{7}$$

$$b - a = \frac{2e^2Qq_{zz}}{3e^2Qq_o}\left(\frac{\eta}{1 - \cot^2\gamma}\right) \tag{8}$$

these parameters to the observed coupling constant and asymmetry parameter. If it is further assumed that there is no π bonding between the ligand and the copper atom then n may be set to zero and these equations used to obtain the bond populations for different ligands. There remains, however, the question of the 3d orbitals. If we assume that the 3d contributions are directly proportional to the 4p population then, for complexes with C_3 symmetry, the effect of the 3d contribution is simply to modify the effective atomic coupling for the 4p electrons. Since this quantity is not directly observable, the 3d effects can thus be directly absorbed into equation (7). If, as is the case for most of the compounds discussed here, the complexes have only C_2 symmetry, then the 3d orbitals also influence the asymmetry parameter, but again if the effect of the 3d orbitals is proportional to the 4p population this may be assimilated into the atomic coupling constant. Equations (7) and (8), containing only one adjustable parameter, may therefore be useful for rationalizing the effect of different ligands on the ^{63}Cu field-gradient tensor.

Before presenting the results for such an analysis we must consider the alternative partial field-gradient approach.[21] Here each ligand is supposed to induce a characteristic point-charge-like field gradient on the central atom. Thus a ligand, L, is assumed to produce a field gradient $2q^L$ along the direction of the vector joining the ligand to the quadrupolar nucleus and $-q^L$ in each of the two directions perpendicular to it. The total field gradient is then the sum of the partial field gradients, q^a and q^b, in which due allowance is made for the relative orientations of the ligands and for the fact that there are two equivalent ligands L^a. With the same axis system we have in this case equations (9)–(11). Appropriate manipulation leads to

$$q_{xx} = 2q^b + 2q^a(3\cos^2\gamma - 1) \tag{9}$$

$$q_{yy} = -q^b + 2q^a(3\sin^2\gamma - 1) \tag{10}$$

$$q_{zz} = -q^b - 2q^a \tag{11}$$

equations (12) and (13) for the partial field gradients in terms of the observed coupling constants.

$$e^2Qq^a = \frac{-e^2Qq_{zz}(3 + \eta)}{6(1 - \cos 2\gamma)} \tag{12}$$

$$e^2Qq^b = -2e^2Qq^a - e^2Qq_{zz} \tag{13}$$

For both these analyses, should the field-gradient y axis lie along the unique Cu–L^b bond then the observed asymmetry parameter must be given a negative sign. Including the result for complex **10** presented here, there are only six three-co-ordinated complexes of Cu^I for which the complete quadrupole-coupling tensor has been determined. In agreement with the premises of both these analyses of the NQR data, the direction of the field-gradient z axis is perpendicular to the plane containing the copper atom and the three ligand atoms not only in **10** but in the three-co-ordinated halide-bridged triphenylphosphine complexes,[4] the monomeric $[CuBr(PPh_3)_2]$,[22] and in the iodide-bridged binuclear dianion $[NPr_4]_2[Cu_2I_4]$.[23] However, the conclusions of these two methods applied to the complete field-gradient tensor of these six compounds, Table 6, are neither internally self-consistent nor, *a fortiori*, in agreement with each other. Thus with both methods there are three reasonably similar estimates for the effect of a terminal triphenylphosphine ligand but, whereas the partial field-gradient model gives two similar appreciations of the effect of a bridging iodide ligand, the orbital model yields ligand-orbital populations in the ratio of 2:1. It must be emphasized, however, that both methods are very approximate and the errors in either partial field gradients or orbital populations must be of the order of ± 10%. A proper evaluation of these two methods therefore requires there to be a larger body of experimental data. The analysis of the ^{63}Cu NQR data would also be facilitated if the complete NQR data for a nucleus bonded to the copper atom, for example Br or I, were also available. There is clearly a need for more Zeeman studies on related complexes, which would lead to an appropriate parameterized method in which the d orbitals are included explicitly.

In Table 7 the resonance frequencies for the iodides reported here are compared with those of the analogous previously reported chlorides and bromides. Except for the complexes of *N*-isopropylimidazolidine-2-thione, which have significantly higher frequencies, the values for a given halogen ligand are all very similar. Even for *N*-isopropylimidazolidine-2-thione the relative frequencies of the three halides conform to the same trend, Cl > Br > I, that was remarked upon for the analogous 2,6-dimethylpyridine complexes,[2,3] while the differences, Cl–Br and Br–I, are essentially independent of the ligand, being both approximately 1.0 MHz. These observations leave little doubt that all these complexes have similar three-co-ordinated structures. It should be noted that the same trend is observed in the quadrupole splitting of the ^{197}Au Mössbauer spectra of two- and three-co-ordinated complexes of gold(I) halides.[24]

Of the four remaining complexes **6** and **8** are known,[8,10] to be planar three-co-ordinated cations with three identical thione ligands, while our NQR results imply that **7** is probably similar to these. The frequency of **8** is similar to a previously reported value obtained at an unspecified temperature.[25] Somewhat lower frequencies (27.390 MHz at 296 K) for an analogous

Table 6 Analysis of the ^{63}Cu NQR data according to equations (7)–(13). The atomic coupling constant was arbitrarily set at −200 MHz

Complex	e^2Qq_{zz}	η	γ	a	b	e^2Qq^a	e^2Qq^b	L^a	L^b
$[Cu_2Cl_2(PPh_3)_3]$	59.08	−0.289	53.7	0.141	0.267	−20.6	−18.0	Cl	P
$[Cu_2Br_2(PPh_3)_3]$	55.82	−0.307	57.1	0.152	0.250	−17.8	−20.3	Br	P
$[Cu_2I_2(PPh_3)_3]$	53.72	−0.332	58.2	0.142	0.239	−16.5	−20.7	I	P
$[CuBr(PPh_3)_2]$	64.58	0.113	63.0	0.368	0.335	−21.1	−22.4	P	Br
10	58.14	−0.36	61.7	0.157	0.256	−16.5	−25.1	S	Cl
$[NPr_4]_2[Cu_2I_4]$	46.5	0.262	58.4	0.318	0.253	−17.5	−11.6	I	I

Table 7 The ^{63}Cu resonance frequencies (MHz at 77 K) of three-co-ordinated complexes, $[CuL_2X]$ (L = thione, X = halide)

Ligand	Cl	Br	I
1-Methylimidazolidine-2-thione	30.768	29.324	28.150
1-Ethylimidazolidine-2-thione	30.296 30.161	29.393	27.948
1-Propylimidazolidine-2-thione	30.046 29.295	28.893	27.462
1-Isopropylimidazolidine-2-thione	32.772[a]	30.343	28.591
Thiocaprolactam	—	30.879	29.486 28.480

[a] At 100 K.

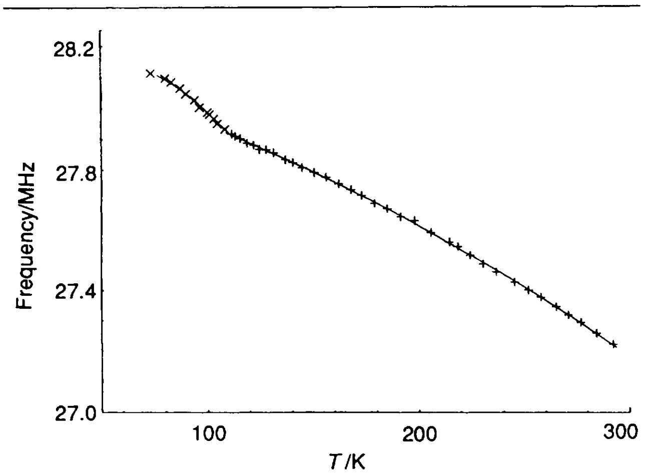

Fig. 5 The temperature dependence of the ^{63}Cu NQR spectrum of complex **1**

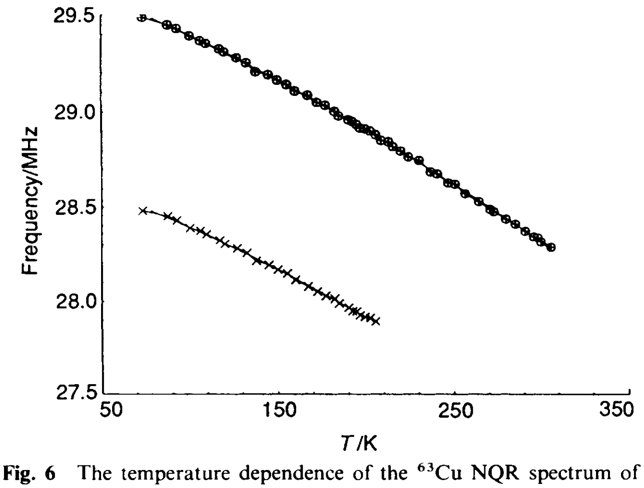

Fig. 6 The temperature dependence of the ^{63}Cu NQR spectrum of complex **5**

three-co-ordinated cation tris(tetramethylthiourea)copper(I) have been reported both for the perchlorate and the tetrafluoroborate.[26] Zeeman studies are unnecessary for these complexes since the near-perfect trigonal symmetry implies both that the asymmetry parameter is zero and that the field-gradient z axis lies along the symmetry axis. For these symmetrical three-co-ordinated cations with $\eta = 0$, analysis of the data according to equation (7) yields the value 0.32 for the population of each of the three equivalent orbitals used to bond to the thione ligands, while from equation (13) the partial field gradient, e^2Qq^a, for the thione ligand is −21.3 MHz. Both these values are very different from those obtained for, respectively, the populations of the two Cu–S orbitals (0.16) or the partial field gradient of the thione ligand (−16.5 MHz) for **10** in Table 6. However, in addition to the considerations outlined above, the analysis of the frequencies of these cations is further complicated by the possibility of more-or-less weak co-ordination of the anion with the cation,[27] but, while the crystallographic data show that this does not occur for **6**, neither the atomic coordinates nor the cation–anion distances are reported for **8** or for tris(tetramethylthiourea)copper(I) tetrafluoroborate.[10] Finally, the two lower frequencies of **9** are in agreement with the structure containing two crystallographically distinct copper atoms and four terminal sulfur atoms and a sulfur bridge.[7]

The temperature dependence of the resonance frequencies of complexes **1** and **5** is shown in Figs. 5 and 6. For **1** the sharp change in the slope at 113 K is probably indicative of a phase change. For **5**, the single resonance line at room temperature is in accord with its crystal structure,[11] also measured at room temperature. At 77 K, however, two distinct resonance frequencies can be seen; one of these persists, with no apparent discontinuity but with gradually increasing intensity, right through to room temperature, whereas the lower-frequency line gradually broadens and weakens with increasing temperature, fading out at around 206 K. This may indicate that, at room temperature, rapid molecular motion results in a dynamic equivalence of two or more distinct copper sites.

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