Copper-63 Nuclear Quadrupole Resonance Frequencies and Molecular Geometries of Three-co-ordinate Complexes of Copper(I) Halides with *N*-Alkylimidazolidinethione and Thiazolidinethione Ligands†

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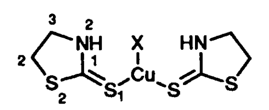
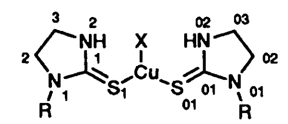
The crystal structures of seven three-co-ordinated complexes of copper(I) halides with thione ligands, $[CuXL_2]$, where L = 1,3-thiazolidine-2-thione and X = Cl or Br, L = *N*-ethylimidazolidine-2-thione and X = Br, L = *N*-isopropylimidazolidine-2-thione and X = Cl or Br, and L = *N*-propylimidazolidine-2-thione and X = Cl or I have been determined. In all complexes, the copper lies in a trigonal-planar environment and the thiazolidine or imidazolidine rings show no major distortion from planarity. Owing to the presence of hydrogen bonding involving H[N(2)], or H[N(02)], and the halogen atom all complexes adopt a W-shaped conformation. The ^{63}Cu NQR frequencies of these complexes, together with those of two other similar complexes whose structures were already available, depend, for a given halide, on the S–Cu–S bond angle, a decrease in angle producing an increase in resonance frequency: $\nu_{Cl} = 28.7 - 0.544\Delta\theta$ and $\nu_{Br} = 26.9 - 0.229\Delta\theta$ MHz, where $\Delta\theta$ is the difference between the S–Cu–S bond angle and 120°. This behaviour has been rationalized in terms of a partial field-gradient model of the resonance frequencies.

We have previously reported studies of the ^{63}Cu NQR spectra of Cu^I complexes with a variety of charges, co-ordination numbers and ligands.[1–9] The ^{63}Cu NQR spectra of the three-co-ordinated complexes, $[CuXL_2]$, of *N*-alkylimidazolidine-2-thiones (L) with cuprous halides[1,2] led us to believe that there was a possible correlation between the L–Cu–L bond angle and the resonance frequency for the complex of a given halide. To investigate this point further we have determined the crystal structures of seven complexes of this type: L = 1,3-thiazolidine-2-thione, X = Cl **1** or Br **2**; L = *N*-ethylimidazolidine-2-thione, X = Br **5**; L = *N*-isopropylimidazolidine-2-thione, X = Cl **6** or Br **7**; and L = *N*-propylimidazolidine-2-thione, X = Cl **8** or I **9**. The crystal structures of two other complexes $[CuClL_2]$ (L = *N*-methylimidazolidine-2-thione **3** or *N*-ethylimidazolidine-2-thione **4**) were already available.[10,11] These results confirm the existence of the correlation and we report here the results of this study.



1 X = Cl
2 X = Br



	X	R		X	R
3	Cl	Me	**7**	Br	Pr^i
4	Cl	Et	**8**	Cl	Pr^n
5	Br	Et	**9**	I	Pr^n
6	Cl	Pr^i			

Experimental

Preparations.—The preparations of the ligands and the Cu^I complexes $[CuXL_2]$ have been reported previously.[1,2] Crystals suitable for X-ray crystallographic studies were obtained by recrystallization from 1,2-dichloroethane (**1**, **2**, **5** and **9**), or acetone (**6** and **7**).

X-Ray Crystallography.—Cell parameters and reflection intensities were measured at room temperature on automatic four-circle diffractometers with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). A summary of the crystal data, intensity measurements and structure refinements is given in Table 1, the atomic coordinates are in Table 2. The structures were solved by direct methods (MULTAN 87[12]) and refined by full-matrix least squares with the XTAL program.[13] Atomic scattering factors and anomalous dispersion terms are taken from ref. 14. Data were corrected for Lorentz and polarization effects and for absorption.[15] Selected geometrical parameters are reported in Table 3.

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

NQR Spectra.—The NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Summary of crystal data, intensity measurement and structure refinement for the Cu^I halide complexes **1, 2, 5–9***

Compound	**1**	**2**	**5**	**6**	**7**	**8**	**9**
Formula	$CuCl(C_3H_5NS_2)_2$	$CuBr(C_3H_5NS_2)_2$	$CuBr(C_5H_{10}N_2S)_2$	$CuCl(C_6H_{12}N_2S)_2$	$CuBr(C_6H_{12}N_2S)_2$	$CuCl(C_6H_{12}N_2S)_2$	$CuI(C_6H_{12}N_2S)_2$
M	337.4	381.8	403.8	387.5	431.9	387.5	478.9
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$Pnma$	$Pbca$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	14.252(3)	14.124(2)	14.616(4)	12.098(2)	7.106(1)	14.104(5)	7.412(2)
b/Å	6.3470(6)	6.4991(4)	7.358(3)	10.689(3)	14.476(2)	14.378(4)	16.452(3)
c/Å	13.500(2)	13.886(1)	14.802(2)	27.568(4)	17.932(6)	19.029(2)	15.443(4)
β/°	105.16(1)	106.912(7)	90	90	95.943(4)	108.77(1)	90.42
U/Å^3	1178.7(3)	1219.5(3)	1602.7(3)	3565(1)	1834.7(7)	3654(2)	1883.1(8)
Z	4	4	4	8	4	8	4
$F(000)$	680	752	816	1616	880	1616	952
Crystal size/mm	0.17 × 0.17 × 0.22	0.17 × 0.23 × 0.26	0.15 × 0.25 × 0.30	0.18 × 0.24 × 0.25	0.15 × 0.17 × 0.40	0.06 × 0.14 × 0.14	0.05 × 0.22 × 0.35
D_c/g cm^{-3}	1.90	2.08	1.67	1.44	1.56	1.41	1.69
$[(\sin\theta)/\lambda]_{max}$/Å^{-1}	0.64	0.64	0.55	0.58	0.58	0.58	0.58
μ(Mo-Kα)/mm^{-1}	2.731	5.715	4.076	1.600	3.566	1.562	3.069
A* (min., max.)	1.432, 1.939	2.315, 3.407	1.752, 2.476	1.294, 1.411	1.631, 1.870	1.180, 1.842	1.165, 1.878
Diffractometer	Philips PW1100	Stoe Stadi-4	Stoe Stadi-4	Stoe Stadi-4	Nonius Cad-4	Stoe Stadi-4	Philips PW1100
No. measured reflections, N_r	2672	1393	4808	2833	2967	4990	3085
No. observed reflections $[\lvert F_o\rvert > 4\sigma(F_o)]$, N_v	1105	1083	754	1704	2041	2148	1757
H atoms	Refined	Refined	Calculated	Refined	Refined	—	Calculated
No. parameters	81	81	122	253	253	312	199
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	1
Maximum Δ/σ	0.0096	0.0049	0.0020	0.21	0.45	0.39	0.04
Maximum and minimum $\Delta\rho$/e Å^{-3}	0.58, −0.78	0.64, −0.62	0.51, −0.48	0.69, −0.69	0.56, −0.56	1.07, −1.26	0.97, −1.08
S	2.27	2.49	1.90	1.85	1.70	4.06	2.90
R, R'	0.035, 0.030	0.030, 0.018	0.041, 0.034	0.044, 0.030	0.049, 0.023	0.093, 0.058	0.053, 0.053

* $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $R' = [\Sigma(w\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$, $S = [\Sigma\{[(F_o - F_c)/\sigma(F_o)]^2\}/(N_r - N_v)]^{\frac{1}{2}}$.

Table 2 Atomic coordinates and population parameters with estimated standard deviations in parentheses for the Cu[I] halide complexes **1**, **2**, **5–7** and **9**

Atom	X/a	Y/b	Z/c
$[CuCl(C_3H_5NS_2)_2]$ **1**			
Cu	$\frac{1}{2}$	0.453 31(9)	$\frac{1}{4}$
Cl	$\frac{1}{2}$	0.093 8(2)	$\frac{1}{4}$
S(1)	0.586 97(6)	0.618 2(1)	0.389 85(7)
S(2)	0.678 45(8)	0.512 1(2)	0.607 32(7)
N	0.609 8(2)	0.231 5(5)	0.476 0(2)
C(1)	0.620 9(2)	0.437 0(5)	0.483 8(2)
C(2)	0.692 8(3)	0.245 4(6)	0.653 3(3)
C(3)	0.640 1(3)	0.106 1(6)	0.567 6(3)
$[CuBr(C_3H_5NS_2)_2]$ **2**			
Cu	$\frac{1}{2}$	0.452 82(9)	$\frac{1}{4}$
Br	$\frac{1}{2}$	0.081 76(8)	$\frac{1}{4}$
S(1)	0.586 81(7)	0.614 8(1)	0.390 14(6)
S(2)	0.682 51(8)	0.521 2(2)	0.605 22(7)
N	0.610 3(2)	0.242 1(5)	0.479 3(2)
C(1)	0.621 7(2)	0.441 3(5)	0.484 2(2)
C(2)	0.696 8(3)	0.263 5(7)	0.655 3(2)
C(3)	0.641 0(3)	0.121 5(6)	0.571 6(3)
$[CuBr(C_5H_{10}N_2S)_2]$ **5**			
Cu	0.305 56(7)	$\frac{3}{4}$	0.335 67(7)
Br	0.145 02(8)	$\frac{3}{4}$	0.344 31(6)
S(1)	0.375 0(2)	$\frac{3}{4}$	0.203 6(2)
N(1)	0.318 9(5)	$\frac{3}{4}$	0.032 8(5)
N(2)	0.209 3(6)	$\frac{3}{4}$	0.128 0(5)
C(1)	0.297 5(7)	$\frac{3}{4}$	0.119 5(6)
C(2)	0.239 3(7)	$\frac{3}{4}$	−0.024 8(6)
C(3)	0.160 6(7)	$\frac{3}{4}$	0.042 5(6)
C(4)*	0.409(1)	0.826(2)	0.000 9(8)
C(5)*	0.440(1)	0.693(3)	−0.068(1)
S(01)	0.394 3(2)	$\frac{3}{4}$	0.456 1(1)
N(01)	0.358 7(6)	$\frac{3}{4}$	0.632 6(5)
N(02)	0.241 3(6)	$\frac{3}{4}$	0.552 4(5)
C(01)	0.330 1(6)	$\frac{3}{4}$	0.551 3(5)
C(02)	0.288 9(8)	$\frac{3}{4}$	0.700 1(6)
C(03)	0.204 1(7)	$\frac{3}{4}$	0.643 8(6)
C(04)*	0.453(2)	0.839(4)	0.656(1)
C(05)*	0.502(2)	0.672(4)	0.680(1)
$[CuCl(C_6H_{12}N_2S)_2]$ **6**			
Cu	0.033 50(5)	0.221 93(6)	0.598 78(2)
Cl	0.037 3(1)	0.169 4(1)	0.519 90(5)
S(1)	0.052 2(1)	0.083 7(1)	0.657 61(5)
N(1)	0.131 5(4)	−0.149 3(4)	0.660 4(2)
N(2)	0.112 7(4)	−0.077 3(4)	0.587 4(2)
C(1)	0.100 9(4)	−0.051 5(4)	0.634 0(2)
C(2)	0.177 5(5)	−0.248 4(5)	0.630 4(2)
C(3)	0.148 6(5)	−0.205 9(6)	0.579 7(2)
C(4)	0.145 0(7)	−0.148 3(6)	0.712 8(2)
C(5)	0.263(1)	−0.140 6(9)	0.726 2(3)
C(6)	0.086 7(8)	−0.253(1)	0.736 0(3)
S(01)	0.007 7(1)	0.421 9(1)	0.618 93(5)
N(01)	−0.138 7(3)	0.584 0(4)	0.582 2(1)
N(02)	−0.108 5(4)	0.422 2(4)	0.536 4(2)
C(01)	−0.082 2(4)	0.478 2(5)	0.577 4(2)
C(02)	−0.218 8(5)	0.596 8(6)	0.543 1(2)
C(03)	−0.183 6(5)	0.496 4(6)	0.507 6(2)
C(04)	−0.141 0(5)	0.659 4(5)	0.626 3(2)
C(05)	−0.219 9(8)	0.606 2(7)	0.662 6(3)
C(06)	−0.163 2(6)	0.795 8(6)	0.614 2(3)
$[CuBr(C_6H_{12}N_2S)_2]$ **7**			
Br	0.308 78(8)	0.374 30(4)	0.315 32(3)
Cu	0.330 81(9)	0.261 10(5)	0.411 47(4)
S(1)	0.156 7(2)	0.264 0(1)	0.507 35(8)
N(1)	−0.157 0(6)	0.352 7(3)	0.537 3(2)
N(2)	−0.056 1(6)	0.395 1(4)	0.431 7(3)
C(1)	−0.026 1(7)	0.339 5(4)	0.490 9(3)
C(2)	−0.297 0(8)	0.421 0(4)	0.507 8(4)
C(3)	−0.226 5(9)	0.449 6(4)	0.434 2(4)
C(4)	−0.165 6(8)	0.307 5(4)	0.609 4(4)
C(5)	−0.350(1)	0.257 1(5)	0.612 3(4)
C(6)	−0.129(1)	0.374 8(6)	0.673 1(5)
S(01)	0.526 1(2)	0.141 0(1)	0.417 28(9)
N(01)	0.825 5(6)	0.096 6(3)	0.345 0(2)
N(02)	0.703 2(6)	0.229 7(3)	0.313 2(3)
C(01)	0.689 9(7)	0.156 4(4)	0.356 5(3)
C(02)	0.942 2(9)	0.130 5(5)	0.289 0(4)
C(03)	0.847 7(8)	0.219 0(5)	0.261 5(4)
C(04)	0.846 6(9)	0.006 2(5)	0.380 3(3)
C(05)	1.052(1)	−0.016 7(5)	0.398 7(4)
C(06)	0.755(1)	−0.067 2(6)	0.329 6(5)
$[CuI(C_6H_{12}N_2S)_2]$ **9**			
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)

* Atomic site refined with a population parameter of 0.5.

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.

Results

NQR Spectra.—The ^{63}Cu NQR spectra and their temperature dependence was observed in the range 77–300 K and the results fitted to the quadratic equation (1). Phase changes occur

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

for **5** at 238, for **4** at 104 and for **6** at 100 K.[1] The presence of two equally intense lines at room temperature for **9**, indicating the presence of two crystallographically inequivalent Cu[I] atoms, is confirmed by the crystal structure.

Discussion

X-Ray Crystallography.—Of all the compounds presented here, three complexes show a crystallographic intramolecular symmetry. The isostructural complexes **1** and **2** (Fig. 1) are located on a C_2 axis with the Cu and X atoms in special positions (Wyckoff sites 4b). In **5**, all atoms, except those of the ethyl substituents at N(1) and N(01), are located on a mirror plane (Wyckoff sites 4c); consequently, the imidazolidine rings and the co-ordination plane are coplanar. It should be noted that for this complex a refinement in space group $Pna2_1$, with the molecule in general position, shows that the chirality/polarity parameter[16] converges to 0.5 which clearly confirms that this structure is centrosymmetric.

Three structures show disorder of one or both substituents at N(1) and/or N(01). As mentioned above, both atomic sites of the ethyl substituent of **5** are located in general positions, out of the mirror plane containing the other atoms of the complex. The refinement of these atomic sites with occupation parameters of 0.5 leads to a coherent geometry of this part of the molecule (Fig. 2). Both complexes with *n*-propyl substituents at N(1) and N(01) (**8** and **9**) exhibit partial or complete disorder of the propyl moieties. In **8**, this disorder is significant and also affects the imidazolidine rings of both independent molecules of the asymmetric unit and therefore we only report here the crystal data (Table 2) and the mean observed geometries about the copper atoms (Table 4). In **9**, only one of the propyl substituents was disordered and successfully resolved in a crossed disorder by splitting two atomic sites (Fig. 3).

In all complexes, the copper lies in a trigonal-planar environment [maximum deviation of the co-ordination plane CuXS(1)S(01) = 0.006 Å for **9**] and the thiazolidine or imidazolidine rings show no major distortion from planarity. All complexes adopt a W-shaped conformation with the substituents at N(1) and N(01) in a *anti* position relative to the Cu–X bond. This particular conformation is due to the presence of hydrogen bonding between H[N(2)], or H[N(02)], and the halogen atom (Table 3). All dihedral angles between the mean plane passing through the five-membered rings and the co-ordination planes lie in the range 0–14°, except for **6** where this angle is 37.8° for one of the imidazolidine rings. Nevertheless hydrogen bonding occurs and the N(02)–H[N(02)] bond direction points to the chlorine atom

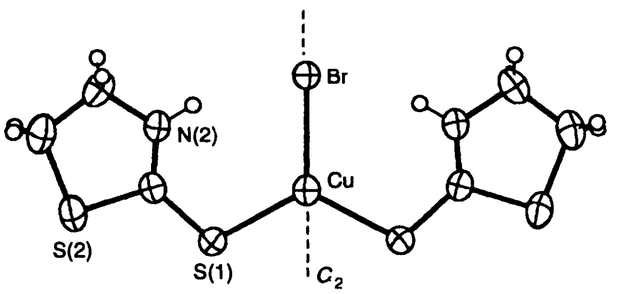


Fig. 1 Structure of the Cu^{I} halide complex **1** with ellipsoids at 50% probability

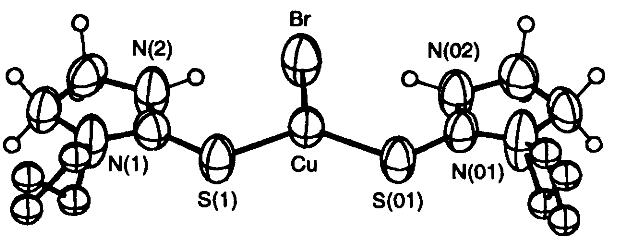


Fig. 2 Structure of the Cu^{I} halide complex **5** showing the disordered ethyl substituents at N(1) and N(01). Ellipsoids are represented with 50% probability and the disordered atoms with arbitrarily fixed atomic radii of 0.2 Å

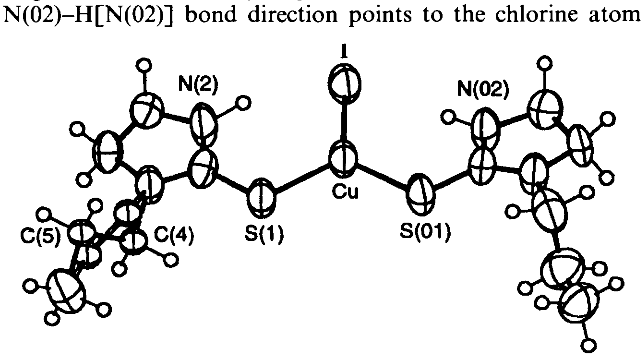


Fig. 3 Structure of the Cu^{I} halide complex **9** showing the partially disordered propyl substituent at N(1). Ellipsoids are represented with 50% probability and the disordered atoms with arbitrarily fixed atomic radii of 0.2 Å

Table 3 Selected geometrical parameters (distances in Å, angles in °) for Cu^{I} halide complexes **1**, **2**, **5**–**7** and **9**

Compound	**1**	**2**	**5**	**6**	**7**	**9**
X	Cl	Br	Br	Cl	Br	I
Cu–X	2.282(1)	2.4116(8)	2.366(2)	2.246(2)	2.372(1)	2.531(2)
Cu–S(1)	2.2297(9)	2.2383(8)	2.206(3)	2.205(2)	2.220(2)	2.227(4)
Cu–S(01)	—	—	2.210(2)	2.230(2)	2.220(2)	2.240(4)
S(1)–C(1)	1.686(3)	1.686(3)	1.69(1)	1.691(5)	1.699(6)	1.71(1)
S(01)–C(01)	—	—	1.696(9)	1.691(5)	1.690(6)	1.69(1)
X–Cu–S(1)	117.98(3)	118.05(2)	120.69(8)	122.85(6)	123.34(6)	122.5(1)
X–Cu–S(01)	—	—	123.13(8)	118.92(5)	124.67(6)	126.0(1)
S(1)–Cu–S(01)	124.03(4)	123.90(4)	116.2(1)	118.23(6)	111.98(7)	111.4(1)
Cu–S(1)–C(1)	107.7(1)	108.8(1)	109.9(3)	109.0(2)	110.8(2)	110.7(5)
Cu–S(01)–C(01)	—	—	109.9(3)	105.2(2)	109.6(2)	110.9(5)
S(1)–C(1)–S(2)	120.7(2)	120.2(2)	—	—	—	—
S(1)–C(1)–N(1)	—	—	123.7(8)	124.1(4)	123.8(4)	125(1)
S(1)–C(1)–N(2)	127.7(2)	128.3(2)	127.0(7)	126.1(4)	125.7(4)	126.3(9)
S(01)–C(01)–N(01)	—	—	126.9(8)	124.5(4)	125.0(4)	125(1)
S(01)–C(01)–N(02)	—	—	124.6(6)	125.1(4)	125.4(4)	125.4(9)
X–Cu–S(1)–C(1)	−11.6(1)	−11.2(1)	0.0	14.3(2)	14.2(2)	−3.0(5)
X–Cu–S(01)–C(01)	—	—	0.0	36.3(2)	13.6(2)	−1.2(5)
Cu–S(1)–C(1)–N(2)	7.6(4)	5.7(2)	0.0	−8.1(5)	−4.7(6)	−5(1)
Cu–S(01)–C(01)–N(02)	—	—	0.0	−14.1(5)	1.5(5)	−4(1)
X···H[N(2)][a]	2.31(3)	2.45(3)	2.30	2.44	2.67	2.55
X···N(2)[a]	3.167(3)	3.281(2)	3.365	3.306	3.504	3.597
Angle between mean planes[b]						
c.p. and fmring	10.9	10.6	0.0, 0.0	13.8, 37.8	13.6, 11.9	5.8, 4.4
fmring and fmring	11.4	14.2	0.0	29.6	19.9	9.8

[a] Mean value for **5**, **6**, **7** and **9**. [b] c.p. = Co-ordination plane [Cu, X, S(1), S(01)]; fmring = thiazolidine or imidazolidine ring.

(Fig. 4). The structure of the corresponding bromide complex **7** is shown in Fig. 5.

NQR Spectra.—Table 4 summarises the NQR frequencies and the bond angles of complexes **1** to **9**. Inspection of these results reveals at once a strong correlation between the S–Cu–S bond angles and the ^{63}Cu NQR frequency, whereas although the S–Cu and the X–Cu bond lengths (Table 3) all show significant variations there does not appear to be any obvious correlation with the NQR data. Fig. 6 shows the correlation for the four chlorides **1**, **3**, **4** and **6** and the three bromides. If we express this correlation in terms of the dependence of the frequency, ν, on the deviation, Δθ°, of the S–Cu–S angle from 120° we obtain the expressions (2) and (3). In view of the lack of

$$\nu_{Cl} = 28.7 - 0.544\Delta\theta \quad (2)$$

$$\nu_{Br} = 26.9 - 0.229\Delta\theta \quad (3)$$

precision of the data for the fifth chloride, **8**, the results for this compound were not included in the correlation but, as can be seen from Fig. 6, the point for this complex lies close to the regression line.

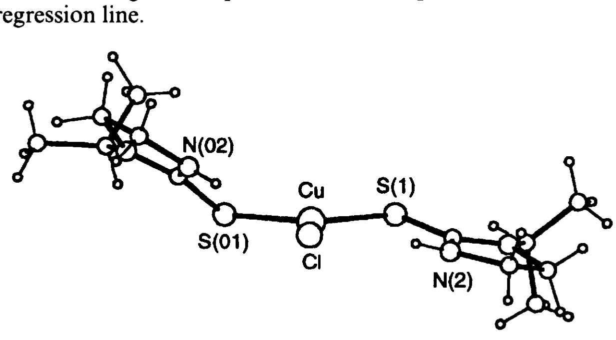


Fig. 4 Structure of the Cu^{I} halide complex **6** showing the N–H bond direction pointing to the chlorine atom. The atomic radii are arbitrarily fixed in order to clarify the diagram

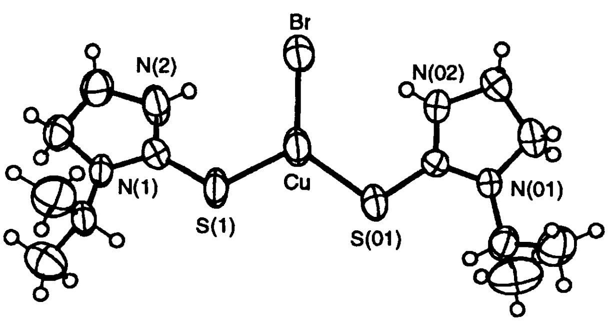


Fig. 5 Structure of the Cu^{I} halide complex **7** with ellipsoids at 50% probability

Table 4 The ^{63}Cu NQR frequencies at 77 and 300 K and bond angles [S–Cu–S] of complexes **1**–**9**

Complex	X	ν_{298}/MHz	ν_{77}/MHz	S–Cu–S/°
1	Cl	26.479	27.400	124.0
4	Cl	28.802	30.296 [a] 30.161 [a]	118.5
6	Cl	30.021	32.722 [b]	118.2
3	Cl	29.481	30.768	119.3
8	Cl	28.388 [c]	29.671 [c]	120.1 [c]
2	Br	26.321	27.059	123.9
5	Br	27.756	29.393 [d]	116.2
7	Br	28.730	30.343	112.0
9	I	26.068	27.462	111.4

[a] Phase transition at 104 K. [b] Phase transition at 100 K. [c] Average for the two different Cu atoms. [d] Phase transition at 238 K.

In accord with our previous studies this equation indicates that the frequency of a chloride is noticeably higher than that of the corresponding bromide, but it also indicates the new result that the chlorides are much more sensitive to the bond angle than are the bromides.

With only one data point for the iodides we cannot, of course, obtain a correlation, but we can at least attempt to see if the resonance frequency is consistent with the data for the chlorides and bromides. All the systems we have studied so far indicate that for a given type of copper(I) halide complex the frequencies lie in the order Cl > Br > I and that the difference between the chloride and bromide is approximately the same as between the bromide and the iodide. On this assumption the frequency for the iodide for a bond angle of 120° is 25.2 MHz and the frequency of **9** is then related to the bond angle by equation (4).

$$\nu_{I} = 25.2 - 0.10\Delta\theta \quad (4)$$

For what it is worth this coefficient of the angular dependence of the iodide is almost exactly in the same ratio to that of the bromide as is the dependence of the bromide to that of the chloride. The conclusion that the frequencies of the iodides are much less sensitive to the S–Cu–S angle than the chlorides or the bromides is confirmed by the fact that the total spread in frequencies [2] of five such thione iodides is only 2 MHz whereas seven chlorides and seven bromides show a range of values of 5.0 and 3.8 MHz respectively.[1] For the purposes of the present discussion we therefore take it as established that the resonance frequencies decrease as the S–Cu–S angle is increased above 120° and that the angular dependence is in the order Cl > Br > I. It has also been established for a wide variety of systems that for a given type of complex the frequencies of the halides vary in the same order.[1–9]

The high polarisability of the Cu^{I} cation together with the participation of both 3d and 4p electrons in the bonding between the central atom and its ligands makes almost impossible even the simple Townes–Dailey [17] analysis of ^{63}Cu NQR frequencies. When this difficulty is compounded with the fact that for a nucleus of spin $\frac{3}{2}$ such as ^{63}Cu the single-resonance frequency is given by equation (5) and that neither

$$\nu_Q = \frac{e^2Qq_{zz}}{2h}\sqrt{1 + \frac{\eta^2}{3}} \quad (5)$$

the coupling constant, e^2Qq_{zz}, nor the asymmetry parameter, η, is known separately, it becomes clear that we must turn to other methods. An alternative technique for accounting for the resonance frequencies of polyco-ordinated nuclei is the partial field-gradient method.[18] In this method the effect of a given

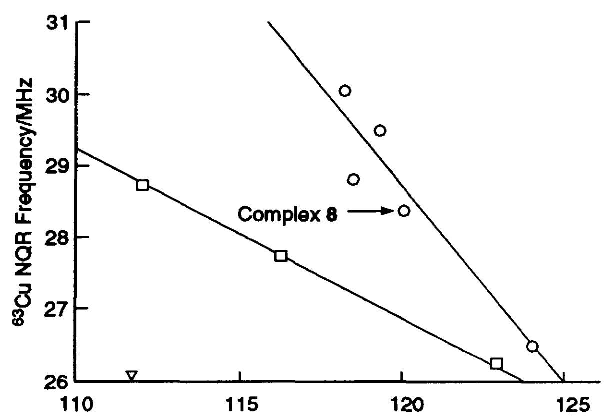
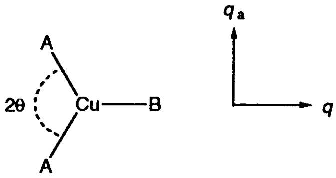


Fig. 6 The ^{63}Cu NQR frequencies (in MHz at 298 K) and S–Cu–S bond angles of three-co-ordinated complexes of copper(I) chlorides (○), bromides (□) and iodides (▽) with thione ligands



Scheme 1

ligand on the field gradient of the central atom is represented by a partial cylindrically symmetrical field-gradient tensor symmetrical about the bond between the central atom and the ligand. The total field-gradient tensor is then given by the sum of these partial tensors. Although we have already demonstrated that for Cu^I complexes it is not possible to characterize a given ligand by a partial field gradient that can be used for a variety of co-ordination numbers of the central atom and a variety of charges of the complex,[2] we have used it with success to account for the difference in resonance frequency between two crystalline modifications of a neutral four-co-ordinated Cu^I complex that had slightly different geometries in the two modifications.[19] It therefore seemed possible that the method could also be useful in this context.

The idealized structure of these complexes is shown in Scheme 1. If the partial field gradients of A and B are represented by a and b respectively, and the A–Cu–A angle by 2θ then q_a and q_b, the components of the field-gradient tensor in the molecular plane perpendicular to and along the Cu–B bond, and q_c, the component perpendicular to the molecular plane are given by equations (6)–(8). For three identical ligands and $\theta =$

$$q_a = 2a(3\sin^2\theta - 1) - b \quad (6)$$

$$q_b = 2a(3\cos^2\theta - 1) + 2b \quad (7)$$

$$q_c = -(2a + b) \quad (8)$$

60° the asymmetry parameter is zero and the q_{zz} direction is q_c, perpendicular to the molecular plane. When the ligands are no longer identical then, provided that the partial field gradients of the ligands A and B are not too different and that 2θ deviates little from 120° the q_{zz} axis will continue to lie along the direction q_c. This is the case for all six complexes with this structure whose field-gradient tensors have been completely determined by Zeeman measurements. For other combinations of ligands the q_{zz} axis may lie along q_a, q_b or q_c and as the parameters are varied it may abruptly switch from one direction to another, as indeed will q_{xx} and q_{yy}. However, for a spin $\frac{3}{2}$ nucleus such as ^{63}Cu it can be shown that there is an exact relationship between the resonance frequency and the three components of the field-gradient tensor that does not depend either on a knowledge of the asymmetry parameter or of the orientation of the directions of these components with respect to the molecular framework. Thus, rewriting equation (5) explicitly in terms of the three field-gradient components we obtain equations (9)–(11); however, $q_{zz} = -(q_{xx} + q_{yy})$ so

$$\nu = \frac{e^2Qq_{zz}}{2\sqrt{3}}\sqrt{3 + \frac{(q_{xx} - q_{yy})^2}{q_{zz}^2}} \quad (9)$$

$$\nu = \frac{e^2Q}{2\sqrt{3}}\sqrt{3q_{zz}^2 + q_{xx}^2 + q_{yy}^2 - 2q_{xx}q_{yy}} \quad (10)$$

$$\nu = \frac{e^2Q}{2\sqrt{3}}\sqrt{q_{zz}^2 + q_{xx}^2 + q_{yy}^2 - 2(q_{xx}q_{yy} - q_{zz}^2)} \quad (11)$$

that $q_{zz}^2 = -q_{zz}(q_{xx} + q_{yy})$, and therefore equation (12) can be

$$\nu = \frac{e^2Q}{2\sqrt{3}}\sqrt{q_{zz}^2 + q_{xx}^2 + q_{yy}^2 - 2(q_{xx}q_{yy} + q_{yy}q_{zz} + q_{zz}q_{xx})} \quad (12)$$

derived. Since each component of the field-gradient tensor occurs in this formula in exactly the same way—either as a square or as a cross product with both of the other components—we may substitute q_a, q_b and q_c for q_{xx}, q_{yy} and q_{zz} without having to worry about the correspondence between the pairs of tensor components. The resonance frequency is therefore a smooth function of q_a, q_b and q_c and thus of a, b and θ, equations (13) and (14). In the present context we are

$$\nu = e^2Q\sqrt{q_a^2 + q_b^2 + q_c^2 - 2(q_aq_b + q_bq_c + q_cq_a)} \quad (13)$$

$$\nu = e^2Q\sqrt{12a^2\cos^2\theta - (12a^2 - 6ab)\cos^2\theta + 4a^2 - 2ab + b^2} \quad (14)$$

interested in the derivative of this expression with respect to θ. This may be straightforwardly obtained as in equation (15).

$$\frac{\partial\nu}{\partial\theta} = \frac{e^2Q[-48a^2\cos^3\theta\sin\theta + (24a^2 - 12ab)\cos\theta\sin\theta]}{2\sqrt{12a^2\cos^4\theta - (12a^2 - 6ab)\cos^2\theta + 4a^2 - 2ab + b^2}} \quad (15)$$

When the ligands are identical then for $\theta = 60°$ $\partial\nu/\partial\theta = 0$, while it can be shown that for this same angle if $a > b$ the derivative is positive and if $a < b$ the derivative is negative. We have already shown that for these complexes the partial field gradients are in the order Cl > Br > I ≈ >C=S.[1,2,20] An approximate value for e^2Qq_a appropriate to the thione ligand is 18 MHz while for Cl, Br and I the values of e^2Qq_b are 26, 22 and 18 MHz respectively. These values imply an angular dependence for thione complexes of −0.206, −0.112 and 0.0 MHz per degree for Cl, Br and I respectively, in reasonable agreement with the experimental values.

Conclusion

The dependence of the ^{63}Cu NQR frequency of three-co-ordinated complexes of copper(I) halides and *N*-alkylimidazolidine-2-thione ligands on the S–Cu–S angle has been demonstrated experimentally and a satisfactory explanation of this effect has been found in the partial field-gradient model.

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