Copper-63,65 Nuclear Quadrupole Resonance of Complexes of Copper(I) Halides with Phosphorus-containing Ligands†

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The ^{63}Cu NQR spectra have been recorded for ten complexes of Cu^I with phosphine and halide ligands that, either on the basis of their previously determined crystal structures or of their analogy to complexes of known structure, were believed to contain three-co-ordinated copper atoms. The NQR resonance frequencies support these attributions and the structure determination of two of the complexes, $[\{CuX(L)\}_2]$ [X = Cl or Br, L = P(C$_6$H$_4$Me-*o*)$_3$], confirms the co-ordination number of three. The NQR results indicated that the previously reported structure for $[Cu_4Br_4(Ph_2PCH_2PPh_2)_2]$ was incorrect and a redetermination of the structure confirmed this conclusion.

The copper(I) cation is well known for its ability to adopt a wide variety of co-ordination numbers so that the molecular formulae of its complexes are not a reliable guide to their molecular structure. While the ultimate tool for structure determination is undoubtedly X-ray crystallography, our previous studies of the ^{63}Cu NQR spectra of such complexes have shown that the NQR technique is a good indication of the co-ordination number of the metal atom. In this context we have previously reported the results of structural and NQR studies of a large number of copper(I) complexes where the ligands are a variety of substituted pyridines[1-3] or thiones.[4,5]

One of the factors that determine the co-ordination number of the metal atom is, of course, the bulk of the ligand. Thus for neutral complexes containing a halogen atom, if the ligand is a relatively unhindered pyridine molecule the metal atom is four-co-ordinated whereas with the heavily-hindered 2,6-dimethylpyridine the co-ordination number is limited to three. In this respect triphenylphosphine appears to be in an intermediate position and both three- and four-co-ordinated copper(I) halide triphenylphosphine complexes have been observed, sometimes even within the same complex. Thus the 1:1 triphenylphosphine:copper(I) halide complexes are tetramers, but while the chloride has the cubane-like structure in which all four copper atoms are four-co-ordinated, the bromide and iodide adopt a stepped chair structure with both three- and four-co-ordinated metal atoms.[6-8] Similarly in the three complex halides $[Cu_2X_2(PPh_3)_3]$ (X = Cl, Br or I) the two Cu atoms are linked by a double halide bridge and one of them achieves four-co-ordination with two of the triphenylphosphine ligands but the other only attains three-co-ordination *via* the remaining ligand.[9,10] In all these complexes this difference between the two Cu atoms is clearly revealed by the two very different ^{63}Cu NQR frequencies,[11,12] the three-co-ordinated site having a frequency of around 30 MHz while the four-co-ordinated site has a value less than half of this. A similar trend was observed for neutral complexes with mixed pyridine and halide ligands[2] while, of course, the copper atom in a tetrahedrally co-ordinated complex with four identical ligands, such as $[Cu(MeCN)_4]ClO_4$, has a resonance frequency of zero.

With a slightly more bulky ligand such as tricyclohexylphosphine the crystal structure of its 1:1 complex with copper(I) chloride, **1**, shows it to be a halide-bridged dimer.[13] The crystal structure of the 1:2 complexes between bis(diphenylphosphino)methane (dppm) and copper(I) bromide or iodide, **5** or **6**, shows them to be dimers whose structures are essentially identical to those of the corresponding triphenylphosphine complexes where adjacent phosphine ligands are linked by the methylene bridge. There are thus two copper atoms co-ordinated to three bridging halides and one phosphorus atom and two copper atoms co-ordinated to two bridging halogen atoms and again one phosphorus atom.[14] For the bromide, however, the crystallographic data indicated that the unit cell contains two crystallographically inequivalent dimeric molecules. The crystal structure of the dichloroethane solvate of the 1:2 complex between dppm and copper(I) chloride, **7**, shows it to have a similar dimeric structure.[15] In the complex bis(tricyclohexylphosphine)copper(I) perchlorate **10** the copper atom is three-co-ordinated to two phosphine ligands and one oxygen atom of the perchlorate anion, which thus acts as a monodentate ligand.[16] On the other hand no crystal structures are available for the complexes of tri-*o*-tolylphosphine, where the steric hindrance of the *ortho*-methyl group might be expected to tilt the balance in favour of the lower co-ordination number. In order to clarify this point and in continuation of a systematic study of the influence of the ligand on the ^{63}Cu NQR resonance frequencies of copper(I) complexes, we report here the results of an NQR study of a number of copper(I) complexes **1**–**10** with phosphine ligands: $[\{CuCl[P(C_6H_{11})_3]\}_2]$ **1**, $[\{CuI[P(C_6H_{11})_3]\}_2]$ **2**, $[\{CuCl[P(C_6H_4Me\text{-}o)_3]\}_2]$ **3**, $[\{CuBr[P(C_6H_4Me\text{-}o)_3]\}_2]$ **4**, $[Cu_4Br_4(dppm)_2]$ **5**, $[Cu_4I_4(dppm)_2]$ **6**, $[Cu_4Cl_4(dppm)_2]\cdot 0.5C_2H_4Cl_2$ **7**, $[Cu_4Cl_4(dppm)_2]\cdot 0.5CH_2Cl_2$ **8**, $[Cu_4Cl_4(dppm)_2]\cdot 0.5CHCl_3$ **9** and $[Cu(ClO_4)\{P(C_6H_{11})_3\}_2]$ **10**. The structures of **1**, **5**–**7** and **10** have been previously reported.[13-16] In addition to the NQR measurements, we report here the results of a crystallographic study of complexes **3** and **4** while the results of our NQR study induced us to repeat the determination of the structure of **5**.

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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 complexes **3**–**5***

Compound	**3**	**4**	**5**
M	806.7	895.6	1342.6
Crystal size/mm	0.24 × 0.24 × 0.24	0.08 × 0.20 × 0.28	0.18 × 0.18 × 0.18
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$Pbca$
a/Å	9.162(1)	9.199(2)	17.808(3)
b/Å	10.470(2)	10.203(2)	16.943(2)
c/Å	20.459(3)	11.257(3)	16.369(4)
α/°		101.56(1)	
β/°	99.24(1)	100.68(1)	
γ/°		99.19(1)	
U/Å^3	1937.1(5)	995.7(4)	4939(2)
Z	2	1	4
F(000)	832	452	2640
D_c/mg mm^{-3}	1.38	1.49	1.81
μ(Mo-Kα)/mm^{-1}	1.349	3.165	5.074
A* (min., max.)	1.297, 1.329	1.255, 2.0	—
$[(\sin\theta)/\lambda]_{max}$/Å^{-1}	0.58	0.58	0.53
No. measured reflections	3125	3127	3459
No observed reflections $[\lvert F_o\rvert > 4\sigma(F_o)]$	2282	2266	1826
No. parameters	217	217	280
Maximum and average Δ/σ	0.60, 0.018	$2 \times 10^{-3}, 4 \times 10^{-4}$	0.04, 0.01
Maximum and minimum $\Delta\rho$/e Å^{-3}	3.3, −3.6	0.91, −1.21	1.31, −1.41
S	2.76	3.07	1.81
R, R'	0.077, 0.045	0.064, 0.040	0.058, 0.030

* Details in common: 298 K; full-matrix refinement; weighting scheme $w = 1/\sigma^2(F_o)$.

Experimental

Preparations.—Complexes **1**–**10** have all been previously described in the literature and were prepared according to the reported methods.[16–19]

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.

X-Ray Crystallography.—Crystals were grown at room temperature from MeOH (**3**) and CH_2Cl_2 (**4** and **5**) solutions. 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 show a decrease in intensities of about 8% during the data collection for complexes **3** and **4**. All reflections were corrected for this drift. Data were corrected for Lorentz-polarization and for absorption[20] for **3** and **4** but not for **5** (μr = 0.91) due to the difficulty in correctly indexing the faces. No extinction corrections were applied. The structures were solved by direct methods[21] and refined by least squares with the XTAL program.[22] Atomic scattering factor and anomalous dispersion terms are taken from ref. 23. All coordinates of the hydrogen atoms have been calculated. The relatively high residual values of $\Delta\rho$ observed for complex **3** are located around the Cu atom. A summary of crystal data, intensity measurements and structure refinements is given in Table 1. The atomic coordinates are reported in Table 2 and selected geometrical parameters in Table 3.

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

Results and Discussion

NQR Spectroscopy.—The ^{63}Cu NQR frequencies of the complexes, together with the ^{81}Br frequency of **5**, are shown in Table 4 while the ^{35}Cl resonances of the solvent molecules in **7**–**9** are shown in Table 5. The temperature dependence of the resonance frequencies was observed in the range 77–300 K and the results fitted by the quadratic equation (1). The coefficients of this equation are shown in the Tables.

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

All the nuclei studied here 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 $0 \leqslant \eta \leqslant 1$

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

and $\eta = (q_{xx} - q_{yy})/q_{zz}$. Even for appreciable values of the asymmetry parameter the coupling constant is approximately equal to twice the resonance frequency, thus for η = 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 ($\approx$1 cm^3) single crystals. We have not, so far, succeeded in obtaining single crystals of any of these complexes with appropriate dimensions. Three measurements of the asymmetry parameters of complexes containing the structural fragment X_2CuP, where X is a bridging chloride, bromide or iodide ligand and P is a tertiary phosphine, are however available. These results, together with a number of others for which only the resonance frequencies are available, as shown in Table 6. All three asymmetry parameters are approximately equal to 0.3, which encourages us to believe that the differences in resonance frequencies that are observed in complexes **1**–**10** reflect differences in the coupling constant rather than in the asymmetry parameter. The crystal structure of **1** has already revealed it to be a dimer and its resonance frequency of 31.4 MHz is very similar both to those of the three-co-ordinated copper(I) in the triphenylphosphine complexes (Table 6) and to those of a variety of three-co-ordinated copper(I) halides with thione ligands.[4,5] In view of the fact that for complex copper(I) halides of similar structure there is a well

Table 2 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for complexes **3**–**5**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) Complex **3**							
Cu	0.075 2(1)	0.425 6(1)	0.448 00(5)	C(10)	−0.087(1)	0.478(1)	0.207 5(6)
Cl	0.076 8(3)	0.393 5(2)	0.558 4(1)	C(11)	−0.153(1)	0.375(1)	0.173 5(6)
P	0.157 8(3)	0.315 5(2)	0.371 0(1)	C(12)	−0.120(1)	0.254(1)	0.196 2(6)
C(1)	0.156 9(9)	0.141 8(8)	0.383 8(4)	C(13)	−0.020(1)	0.235(1)	0.253 6(5)
C(2)	0.037 5(9)	0.082 2(8)	0.405 9(4)	C(14)	0.089(1)	0.581(1)	0.297 4(5)
C(3)	0.045(1)	−0.049 8(9)	0.417 7(5)	C(15)	0.349 0(9)	0.348 8(8)	0.359 6(5)
C(4)	0.167(1)	−0.119 6(9)	0.408 4(5)	C(16)	0.461(1)	0.352 8(9)	0.413 6(5)
C(5)	0.287(1)	−0.060 3(9)	0.386 8(5)	C(17)	0.603(1)	0.379(1)	0.401 6(6)
C(6)	0.283(1)	0.069 7(9)	0.375 2(5)	C(18)	0.634(1)	0.401(1)	0.338 8(6)
C(7)	−0.101(1)	0.153 1(9)	0.413 9(5)	C(19)	0.519(1)	0.395 3(9)	0.285 2(5)
C(8)	0.045(1)	0.339 3(9)	0.289 8(4)	C(20)	0.379(1)	0.369 9(9)	0.295 9(5)
C(9)	0.014(1)	0.464 9(9)	0.265 8(5)	C(21)	0.438(1)	0.324(1)	0.483 3(5)
(*b*) Complex **4**							
Cu	0.120 6(1)	0.105 9(1)	0.605 34(9)	C(10)	0.694(1)	0.175 4(9)	0.719 6(9)
Br	0.056 9(1)	0.090 5(1)	0.383 17(8)	C(11)	0.768 3(9)	0.195 7(9)	0.841(1)
P	0.280 7(2)	0.263 4(2)	0.755 1(2)	C(12)	0.704(1)	0.241 1(9)	0.936 8(8)
C(1)	0.294 7(9)	0.438 2(8)	0.731 3(7)	C(13)	0.561 3(9)	0.263 5(8)	0.910 6(7)
C(2)	0.160(1)	0.482 6(9)	0.687 2(7)	C(14)	0.472 7(9)	0.189(1)	0.554 1(9)
C(3)	0.173(1)	0.613(1)	0.669 4(9)	C(15)	0.226 7(8)	0.273 7(8)	0.903 0(6)
C(4)	0.313(2)	0.699(1)	0.695(1)	C(16)	0.210 6(8)	0.157 6(8)	0.952 9(7)
C(5)	0.443(1)	0.654(1)	0.735 7(9)	C(17)	0.157 9(9)	0.170 2(9)	1.064 3(9)
C(6)	0.434(1)	0.526 9(9)	0.756 1(8)	C(18)	0.125(1)	0.288(1)	1.124 4(8)
C(7)	0.005 9(9)	0.393 6(8)	0.660 6(7)	C(19)	0.143 8(9)	0.401 9(9)	1.074 5(8)
C(8)	0.481 0(8)	0.242 2(7)	0.786 8(8)	C(20)	0.195 8(8)	0.391 7(8)	0.966 1(7)
C(9)	0.551(1)	0.202 4(8)	0.688 8(8)	C(21)	0.249 8(9)	0.025 5(8)	0.898 2(7)
(*c*) Complex **5**							
Br(1)	0.478 02(7)	0.038 27(7)	0.607 44(7)	C(11)	0.456 1(8)	0.419 6(7)	0.694(1)
Br(2)	0.642 22(8)	−0.120 04(8)	0.567 28(9)	C(12)	0.505 7(8)	0.363 4(8)	0.723 0(7)
Cu(1)	0.594 65(8)	0.012 06(8)	0.518 51(9)	C(13)	0.537 5(8)	0.310 5(7)	0.670 1(8)
Cu(2)	0.471 21(8)	0.146 40(8)	0.499 2(1)	C(14)	0.720 6(7)	0.143 0(7)	0.425 2(7)
P(1)	0.676 7(2)	0.110 2(2)	0.520 6(2)	C(15)	0.778 3(7)	0.195 5(8)	0.426 4(7)
P(2)	0.555 4(2)	0.238 5(2)	0.517 4(2)	C(16)	0.809 4(7)	0.218 3(8)	0.353(1)
C(1)	0.639 9(6)	0.200 5(6)	0.566 4(6)	C(17)	0.786 7(9)	0.186(1)	0.281(1)
C(2)	0.758 5(6)	0.088 9(6)	0.584 7(7)	C(18)	0.734(1)	0.133 5(9)	0.280 6(8)
C(3)	0.802 0(7)	0.025 7(7)	0.562 6(7)	C(19)	0.698 4(8)	0.110 1(8)	0.353 1(9)
C(4)	0.864 8(7)	0.005 3(7)	0.607 0(9)	C(20)	0.587 9(8)	0.298 9(7)	0.431 2(7)
C(5)	0.880 7(7)	0.046 6(9)	0.677 9(9)	C(21)	0.655 5(8)	0.341 6(8)	0.433 5(9)
C(6)	0.838 9(9)	0.107 1(9)	0.700 3(9)	C(22)	0.675(1)	0.386 7(9)	0.369(1)
C(7)	0.775 5(8)	0.127 2(8)	0.653 8(9)	C(23)	0.626(2)	0.390(1)	0.301(1)
C(8)	0.521 4(7)	0.314 0(7)	0.589 3(7)	C(24)	0.561(1)	0.351(1)	0.298(1)
C(9)	0.471 9(7)	0.369 5(7)	0.557 4(8)	C(25)	0.541 9(8)	0.303 6(8)	0.365(1)
C(10)	0.440 3(7)	0.423 2(7)	0.610(1)				

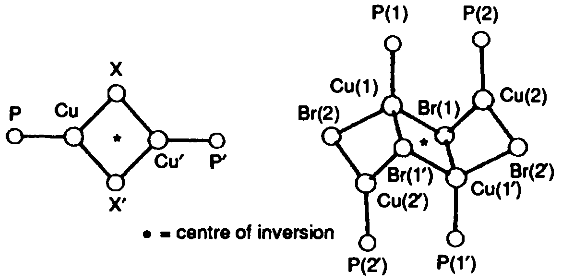
established trend, also observed in the quadrupole splitting of the Mössbauer spectra of analogous gold(I) complexes,^{24} that the resonance frequencies lie in the order Cl > Br > I, the resonance frequency of **2** is in complete accord with it being likewise an iodide-bridged dimer. We were unable to detect a resonance from samples of the bromine analogue of **1** and **2**.

Only one resonance frequency in the neighbourhood of 30 MHz for complex **3** or **4** could be detected; this is a strong indication that these complexes, too, are halide-bridged dimers. The absence of an NQR frequency, particularly one in the region of 13 MHz where our spectrometer is not particularly sensitive, is not, however, a proof of structure. As reported below, however, the crystallographic results confirm the dimeric structure in both cases and the NQR frequencies once more conform to the trend Cl > Br. We were, however, unable to detect a resonance from the corresponding iodide.

For complex **5** we expected to observe two resonances around 30 MHz and two resonances at a much lower frequency. While we were not unduly surprised at the absence of any low-frequency resonances [the previous study of the triphenylphosphine copper(I) bromide and iodide also failed to reveal the resonance of the four-co-ordinated copper atoms], the observation of only one ^{63}Cu resonance of around 29 MHz, over the whole temperature range from 77 to 300 K, was clearly incompatible with the published structure. The single high-frequency resonance of the iodide, **6**, is however completely compatible with the published structure. This result prompted us to determine the crystal structure of our sample of **5**, reported below. These results confirmed the basic dimeric structure but also indicated that the space group had been incorrectly attributed^{14} and that the data could be successfully analysed in terms of a structure with only one type of complex molecule in the unit cell. The crystal structure of the dichloroethane solvate of the complex between copper(I) chloride and bis(diphenylphosphino)methane, **7**, shows it to have a similar dimeric structure^{15} and the ^{63}Cu NQR frequency at room temperature is again completely compatible with this, as are the frequencies of the solvates with methylene chloride and with chloroform, **8** and **9**. At 77 K, however, there are two distinct ^{63}Cu resonance frequencies for **7** so that the low-temperature structure cannot be the same as that determined at room temperature. The temperature dependence of the NQR spectrum, Fig. 1, shows that a first-order phase change occurs at 202 K.

The crystallographic study of complex **7** indicated a disordered structure for the solvent and was unable to localize the carbon atoms of the dichloroethane molecules. It did, however,

Table 3 Selected bond lengths (Å) and angles (°) for complexes **3**–**5**



	3 (X=Cl)	**4** (X=Br)		**3** (X=Cl)	**4** (X=Br)
Cu ··· Cu′	3.130(2)	3.111(1)	X–Cu–X′	94.8(1)	100.06(4)
X ··· X′	3.403(3)	3.712(2)	Cu–X–Cu′	85.2(1)	79.94(5)
Cu–X	2.281(3)	2.428(1)	X–Cu–P	133.6(1)	129.85(8)
Cu–X′	2.342(3)	2.416(1)	X′–Cu–P	131.2(1)	129.92(8)
Cu–P	2.183(3)	2.198(2)	Φ[a]	59.6(2)	63.3(3)
				122.0(3)	121.4(2)
				63.4(3)	69.1(2)
P–C_{phenyl}[b]	1.834(9)	1.841(9)			

Complex **5**

Cu(1) ··· Cu(1′)	3.449(2)	Cu(2)–Br(2′)	2.337(2)	Br(1)–Cu(1)–Br(2)	104.18(7)
Cu(1) ··· Cu(2)	3.180(2)	Br(1) ··· Br(1′)	3.830(1)	Br(1)–Cu(1)–Br(1′)	95.98(6)
Cu(1) ··· Cu(2′)	2.944(2)	Br(1) ··· Br(2′)	3.832(2)	Br(2)–Cu(1)–Br(1′)	97.36(6)
Cu(1)–Br(1)	2.575(2)	Cu(1)–P(1)	2.215(3)	Cu(1)–Br(1)–Cu(2)	76.67(6)
Cu(1)–Br(2)	2.523(2)	Cu(2)–P(2)	2.184(3)	Cu(1)–Br(1)–Cu(1′)	84.02(6)
Cu(1)–Br(1′)	2.579(2)	P–C_{phenyl}[b]	1.84(1)	Cu(2)–Br(1)–Cu(1′)	70.02(6)
Cu(2)–Br(1)	2.552(2)			Cu(1)–Br(2)–Cu(2′)	74.46(7)

[a] Dihedral angle between Cu_2Cl_2 plane and phenyl group. [b] Mean values.

Table 4 Copper-63 NQR frequencies and their temperature dependence. Also shown is the ^{81}Br frequency for complex **5**. In all cases the corresponding ^{65}Cu frequencies were equal to 0.925 times that of the corresponding ^{63}Cu nucleus, while the ^{79}Br frequency was observed at 1.197 times that of the ^{81}Br nucleus

Complex	ν_{77}/MHz	ν_0/MHz	A/kHz K^{-1}	B/Hz K^{-2}
1	31.473	31.838	−4.284	−5.187
2	29.408	29.810	−4.982	−1.787
3	32.592	33.056	−5.300	−7.698
4	30.884	31.253	−4.291	−7.137
5	28.883	29.226	−3.625	−9.942
	50.148[a]	50.841	−8.430	−4.867
6	26.230	26.637[b]	−2.479	−36.388
7	30.439	30.864[c]	−5.196	−2.654
	30.069	30.298[c]	−2.324	−8.207
		31.201[d]	−6.787	−0.929
8	30.127	30.254	−1.187	−9.030
9	30.337	30.512	−1.376	−11.461
10	37.598	37.465[e]	9.661	−103.126

[a] For ^{81}Br. [b] $77 \leqslant T \leqslant 153$ K. [c] $77 \leqslant T \leqslant 202$ K. [d] $202 \leqslant T \leqslant 300$ K. [e] $77 \leqslant T \leqslant 94$ K.

Table 5 Chlorine-35 NQR frequencies of the included solvent molecules in complexes **7**–**9** and their temperature dependence

Complex	ν_{77}/ MHz	$\nu/_0$ MHz	A/ kHz K^{-1}	B/ Hz K^{-2}	Range (K)
7	35.166	35.502	−29.96	−18.14	77–146
	34.828	35.098	−2.564	−11.26	
8	35.220	35.082	11.51	−127.8	77–156
9	38.234	38.012	12.11	−120.1	77–100
	37.523	36.936	20.88	−171.8	

Table 6 Copper-63 NQR frequencies and asymmetry parameters of three-co-ordinated copper(I) complexes having one phosphine and two bridging halide ligands

Complex	ν_{298}/(MHz	η	Ref.
$[Cu_2Cl_2(PPh_3)_3]$	29.95	0.289	12
$[Cu_2Cl_2(PPh_3)_3]\cdot 0.5CHCl_3$	29.94		11
$[Cu_2Cl_2(PPh_3)_3]\cdot C_6H_6$	30.37		11
$[Cu_2Br_2(PPh_3)_3]$	28.36	0.307	12
$[Cu_2Br_2(PPh_3)_3]\cdot CHCl_3$	28.65		11
$[Cu_2I_2(PPh_3)_3]$	27.35	0.332	12
$[Cu_2I_2(PPh_3)_3]\cdot 0.5C_2H_4Cl_2$	27.39		11
$[\{CuBr(PPh_3)\}_4]\cdot 2CHCl_3$	28.09		11
$[\{CuI(PPh_3)\}_4]\cdot 2CHCl_3$	26.09		11

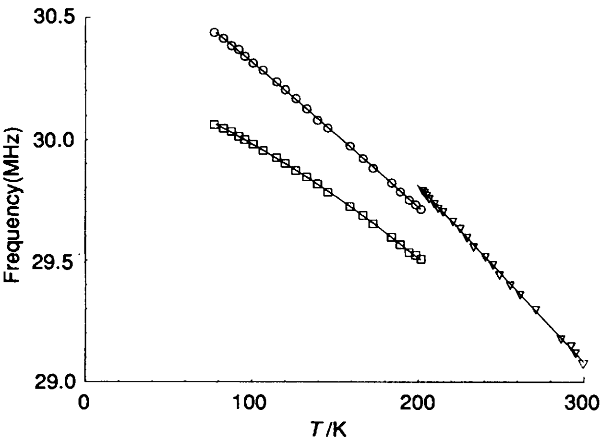


Fig. 1 The temperature dependence of the ^{63}Cu NQR frequencies of complex **7**

indicate that there were two crystallographically independent CH_2Cl groups and, although we know that the crystal structures of the low- and high-temperature phases are not the same, we do observe two distinct ^{35}Cl resonances at 77 K. These resonances, however, fade out at 146 K, presumably

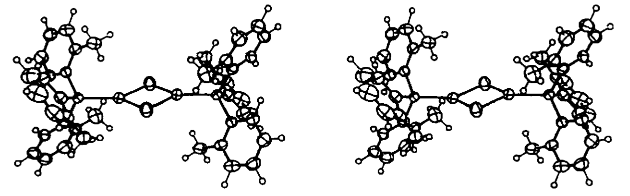


Fig. 2 Stereoview of the copper(I) chloride complex **3**. Ellipsoids are represented with 50% probability. Complex **4** has a structure that is essentially identical (see Table 3). The atomic numbering for both complexes is given in Table 3, where the molecular fragment is oriented exactly as in this Figure

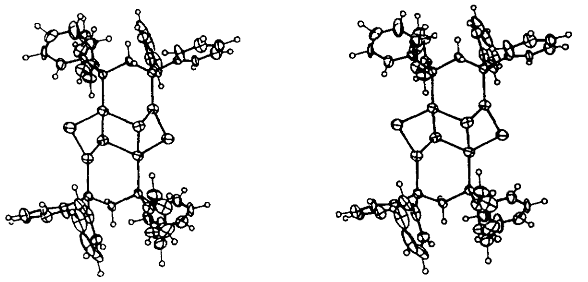


Fig. 3 Stereoview of the copper(I) bromide bis(diphenylphosphino)-methane complex **5**. Ellipsoids are represented with 50% probability. The atomic numbering is given in Table 3

owing to rapid molecular reorientation. It is possible that rapid reorientation of the solvent molecule is partly responsible for the phase change at 202 K. However, while the ^{35}Cl resonances of the solvent molecules in **8** and **9** also fade out at 156 and 100 K respectively, the ^{63}Cu nucleus shows just one resonance frequency throughout the whole temperature range with no evidence of a phase change. For both these complexes the solvent molecule is located at a site containing a two-fold symmetry element, as evidenced by the fact that there is only one ^{35}Cl signal for **8** and that the two signals for **9** have relative intensities of approximately 2 : 1.

We were unable to observe any NQR signals from samples of complex **7** from which the solvent had been removed. On the other hand recrystallization of either **5** or **6** from any of the three chlorinated solvents failed to produce solvated forms of these complexes, as evidenced both by the values of the ^{63}Cu resonance frequencies of the recrystallized samples and by the absence of ^{35}Cl resonances corresponding to the solvent molecules.

The crystal structure of complex **10** shows clearly that the metal atom is three-co-ordinated, with a P–Cu–P bond angle of 144.46° and a distance of only 2.22 Å to one of the oxygen atoms of the adjacent perchlorate anion, while the IR spectrum of the perchlorate anion confirms that it is acting as a monodentate ligand.[16] Its ^{63}Cu NQR frequency is noticeably greater than those of the halides but, insofar as the electronegativity of the perchlorate anion can be considered to be greater than that of the halides, it respects the trend Cl > Br > I that has already been noted.

X-Ray Crystallography.—The halide-bridged dimeric structures of **3** and **4** are very similar to that of **1** (Fig. 2). Similar dimeric structures of 1 : 1 complexes between mesityldiphenylphosphine and the copper(I) halides have also been reported recently.[25] Complex **5** has previously been described[14] as monoclinic, space group $P2_1/c$. In this description, two independent copper(I) bromide bis(diphenylphosphino)methane molecules are necessary to describe the structure. In fact the metric of the unit-cell parameters is orthorhombic (CREDUC[26]) and an investigation with the program MISSYM[27] indicated that the structure contained two supplementary glide planes. The bromide complex **5** is in fact isostructural with **6** and we report here its crystal structure in the space group *Pbca* (Fig. 3).

Conclusion

The ^{63}Cu NQR frequencies of three-co-ordinated copper(I) halides, where two of the ligands are bridging halogen atoms and the third ligand is a phosphine, fall in the range 26–32 MHz. For a given ligand the frequencies depend on the halogen in the sense Cl > Br > I, a trend that is now well established for a wide variety of copper(I) complexes. The NQR frequencies of **1**, **6**, **7** and **10** are in accord with their published crystal structures but that of **5** indicated, in contradiction to the published structure, that the complex contained only one crystallographically distinct molecule in the unit cell. Our determination of the structure of **5** confirms the NQR result and indicates that the space group was incorrectly assigned in the original crystallographic investigation. In confirmation of the conclusions of the NQR study, the crystal structures of **3** and **4** show them to be halide-bridged dimers, while the NQR frequency of **2** indicates that it, too, is a halide-bridged dimer, isostructural with **1**.

Acknowledgements

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