^{63,65}Cu and ^{79,81}Br NQR Studies of Halogenocuprate Complexes of Triphenylphosphine *

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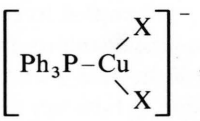
^{63,65}Cu and ^{79,81}Br spectra of halogenocuprate (I) complexes containing $[CuPPh_3X_2]^-$ (X = Cl, Br, I) anions with different cations were recorded in the range 77 K – 300 K. The results confirm the previous trend that, for a given ligand, ^{63}Cu NQR frequencies are in the order Cl > Br > I. ^{63}Cu NQR frequencies in $[CuPPh_3X_2]^-$ are compared with those in neutral $Cu(Ph_3)_2X$ (X = Cl, Br) complexes and with the $[CuX_2]^-$ (X = Cl, Br) anions. ^{81}Br frequencies are compared with those of other three-coordinate Cu(I) complexes.

Key words: ^{63}Cu; ^{81}Br; Cu(I), Halogenocuprate.

Introduction

The difficulties of providing a simple interpretation of the ^{63,65}Cu NQR frequencies of Cu(I) complexes have prompted us to a widely-ranging investigation of such complexes with a variety of coordination numbers, ligands and charges [1–8]. For phosphine ligands the ^{63,65}Cu NQR frequencies of complexes of the cuprous halides have been observed for neutral complexes with two-, three- and four-coordinated copper atoms [4, 5, 9–11] so that the recent publication [12] of the preparation and structure, **I**, of three-coordinated anionic Cu(I) complexes of triphenylphosphine with cuprous halides, $[M]^+ [Ph_3PCuX_2]^-$,



provided us with the opportunity of investigating the effect of a negative charge, in extension of our previous studies of the effect of a positive charge on the complexes involving a hindered pyridine such as 2,6-lutidine as a ligand [6, 7]. We therefore report the ^{63}Cu NQR frequencies of ten such complexes with examples of the three halogens Cl, Br and I and with a variety of cations.

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Experimental

The complexes **1**, **3**, **4** and **10** (cf. Table 1) were prepared as in [12] while the remaining, previously-unreported, complexes were prepared by a simple extension of the preparative method. 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.

Results and Discussion

Table 1 reports the ^{63}Cu resonance frequencies, measured at 77 K, for the ten complexes, together with the ^{81}Br frequencies for **3** and **5**. In all cases the corresponding ^{65}Cu resonances were observed at frequencies equal to 0.925 times those of the ^{63}Cu resonances and for ^{79}Br at 1.197 times those of ^{81}Br. The temperature dependence of the ^{63}Cu resonance frequencies was observed over the temperature range 77–300 K and the frequencies fitted to a quadratic equation

$$\nu_T = \nu_0 + AT + BT^2 .$$

The coefficients of this quadratic are shown in Table 1. The evolution of all the NQR spectra is continuous throught the whole temperature range, with no evidence of phase-changes. The coefficients A and B

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Table 1. ^{63}Cu resonance frequencies of complex halocuprates, $M^+[Ph_3PCuX_2]^-$, and their temperature dependence

M^+	X	No.	ν_{77} (MHz)	ν_0 (MHz)	A(kHz K^{-1})	B(Hz K^{-2})
$(C_2H_5)_4N^+$	Cl	**1**	35.278	35.629	−3.897	−6.548
$(C_2H_5)_4P^+$	Cl	**2**	35.120	35.382	−2.711	−8.586
$(C_2H_5)_4N^+$	Br	**3**	33.197 48.201[a] 49.124[a]	33.490	−3.154	−7.552
$(n\text{-}C_3H_7)_4N^+$	Br	**4**	31.150[b]			
$(C_2H_5)_4P^+$	Br	**5**	33.092 47.664[c] 48.867[c]	33.380	−3.118	−7.227
$(CH_3Ph_3)P^+$	Br	**6**	32.289	32.615	−3.616	−6.377
$(C_2H_5Ph_3)P^+$	Br	**7**	32.105	32.544	−5.407	−2.388
$(n\text{-}C_4H_9Ph_3)P^+$	Br	**8**	31.238[b]			
$(PhMe_3)N^+$	Br	**9**	33.728	34.044	−3.426	−6.999
$(n\text{-}C_3H_7)_4N^+$	I	**10**	29.710	30.112	−5.037	−0.817

[a] ^{81}Br resonance. At 298 K the resonance frequencies were 46.504 and 47.653 MHz, respectively.
[b] Measured at 298 K, the resonance signal faded out as the temperature was lowered.
[c] ^{81}Br resonance. At 298 K the resonance frequencies were 45.942 and 47.442 MHz, respectively

Table 2. ^{63}Cu and ^{81}Br resonance frequencies of three- and two-coordinated cuprous halides with phosphine ligands

Complex	ν_{77} (MHz)	Reference
$(Ph_3P)_2CuCl$	33.17[a]	[9]
$(Ph_3P)_2CuBr$	33.93 56.63[b]	[11]
$[CuI_3]^-$	26.29[a]	[13]
$(o\text{-Tolyl}_3PCuBr)_2$	32.592	[4]
$(o\text{-Tolyl}_3PCuI)_2$	30.884	[4]
$(Cyclohexyl_3PCuCl)_2$	31.473	[4]
$(Cyclohexyl_3PCuI)_2$	29.408	[4]
$(Cu_2Br_4)^{2-}$	31.2[c] 37.940[b] 45.406[b]	[1]
$(Cu_2I_4)^{2-}$	25.4[d]	[1]
$Mesityl_3PCuBr$	35.475	[5]
$(CuCl_2)^-$	30.9	[14]
$(CuBr_2)^-$	28.85 63.8[b]	[14]

[a] Measured at room temperature.
[b] ^{81}Br resonance frequency.
[c] Average of nine compounds.
[d] Average of eight compounds.

show no evidence of any unusual mobility of the copper-containing fragment and, indeed, are remarkably similar for all ten complexes studied. Since no discontinuities were observed in the temperature dependence of the ^{63}Cu resonances, and the frequency at 298 K was, as usual, 1–2 MHz lower than at 77 K, a complete temperature dependence was not obtained for the ^{81}Br resonances in **3** and **5.**

In Table 2 are shown the NQR frequencies of a number of the neutral three-coordinate species $(Ph_3)_2PCuX$, [9, 11], the neutral halogen-bridged three-coordinate species $[(o\text{-Tolyl})_3PCuX]_2$, [4], the triiodocuprate(I) anion, CuI_3^{2-}, [13], and the halogen-bridged dimeric dianions $(CuX)_2^{2-}$, [1], together with the results for the two-coordinated complex (2,4,6-trimethylphenyl)$_3$PCuBr [5] and the CuX_2^- anions [14] that are relevant to the present study.

The effect of the halogen atom on the ^{63}Cu resonance frequency follows the well-established trend Cl > Br > I, the fact that there are two halogen atoms in these complexes being no doubt responsible for the trend being particularly noticeable. The frequencies of the halocuprate complexes are so similar to those of the analogous neutral $(Ph_3P)_2CuX$ complexes and to the binuclear halogen-bridged $(R_3PCuX)_2$ species that, at first sight, one would be tempted to conclude that the bonding of the phosphine ligand to the Cu(I) atom is very similar to that of the halogen anions. A completely opposite conclusion is however obtained from a consideration of the change in coordination number from two to three. The bromocuprate anion considered here may be thought of as arising from the addition of a Br^- anion to R_3PCuBr or from the addition of an R_3P ligand to $CuBr_2^-$. Reference to the data in Table 2 shows that in the first case the change results in a decrease in frequency of 2.2 MHz while the second process produces an increase of over 4 MHz. As has been pointed out by Bowmaker et al. [15], on the one hand the field-gradient at the copper nucleus arises from contributions of electrons in both the 3d and the 4p orbitals while on the other the radial parts of these orbitals – and thus their contribution to the field-gradient – are dependent both of the nature of the ligand and of the coordination number of the copper atom. To compound these difficulties, the 3d

contribution, essentially arising from a hole in the $3d^{10}$ shell – is of opposite sign to that of the electrons that occupy the 4p acceptor orbital. The similarity of the resonance frequencies of the neutral monomers and bridged dimers to those of the negatively-charged species discussed here is thus undoubtedly due to cancellation of different effects on these two sources of the electronic field-gradient. This question is discussed in greater depth in [16].

We were unable to observe ^{81}Br resoances from **4**, where the crystal structure is known [12]. In **4**, the two Cu–Br bonds are slightly different while the two resonance frequencies for **3** and **5** indicate that a similar situation prevails in these complexes. In contrast to the ^{63}Cu frequencies, the ^{81}Br frequencies of $[Ph_3PCuBr_2^-]$ are very different from those of $(Ph_3)_2PCuBr$. The frequency is, as expected, lower for the species with the higher negative charge on the halogen atom. The fact that the ^{81}Br frequency of $CuBr_2^-$ is so much higher than that of $[Ph_3PCuBr_2^-]$ is, however, surprising and implies that the Cu–Br bond is weaker in the phosphine complex. This hypothesis is born out by the values of the Cu–Br bond-lengths (Å): **4** 2.384 and 2.349 [12], $(Ph_3)_2PCuBr$ 2.346 [17]; $CuBr_2^-$ 2.226 [18].

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