# $^{63}$Cu NQR Studies of Two- and Three-coordinated Complexes of Cu(I) with Siloxyl Ligands*

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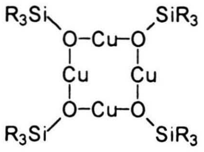
We report the $^{63}$Cu NQR spectra of seven two- and three-coordinated complexes with the siloxyl ligand, $R_3SiO^-$. The frequencies are compared to those of other two- and three-coordinated species, and it is demonstrated that the partial field gradient of the $R_3SiO^-$ group is very similar to that of $Cl^-$.

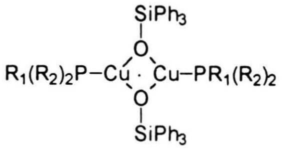
## Introduction

Whereas we have extensively reported the $^{63}$Cu NQR spectra of complexes of Cu(I) with ligands having nitrogen, sulphur, phosphorus, chlorine, bromine and iodine as the donor atom, [1], we had not so far been able to observe resonances from complexes with ligands having first-row donors other than nitrogen. In particular we were unable to observe resonances from the two-coordinated complexes, $(C_6H_5COOCu)_4$ and $(^tBuOCu)_4$, and the three-coordinated complexes, $(Ph_3P)_2CuOOCR$ and $(RCOCH{=}C(O)R)CuMe_3P$, where the oxygen atom is bonded to carbon.

Our lack of success with organo-oxygen donors prompted us to turn our attention to oxygen atoms bonded to other non-metallic residues, and we report here the results for three different types of complex, **I–III**, where at least one of the ligands is a siloxy group, $R_3SiO^-$.



**I**



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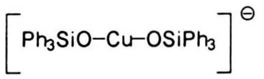

$[Ph_3SiO{-}Cu{-}OSiPh_3]^{\ominus}$

**III**

**Ia**, R = phenyl; **Ib** = **Ia** + toluene, **Ic**, R = *t*-butyl; **IIa** $R_1 = R_2 = n$-butyl; **IIb**, $R_1$ = phenyl, $R_2$ = methyl; **IIc** $R_1 = R_2 = n$-propyl; **III**, counter-ion K(crown), 0.5 toluene.

## Experimental

### Preparations

All manipulations were carried out using standard methods under a nitrogen atmosphere and the complexes prepared according to the literature method [2]. The solvents were dried with an appropriate reagent: sodium for hexane, toluene, tetrahydrofuran; sodium hydride for dichlormethane. Starting materials; $Ph_3SiOH$, $Me_2{}^tBuSiOH$, KH, CuCl, 18-crown-6-ether, mesitylmagnesium bromide, $^nPr_3P$, $^nBu_3P$ and $Me_2PhP$ were commercial products (Aldrich).

### NQR

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-

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Packard 2802 digital thermometer and varied between 77 K and room temperature with an Artronix 5301-E temperature controller.

## Results and Discussion

The $^{63}$Cu NQR spectra and their temperature dependence were observed in the range 77 K – 300 K and the results fitted to a quadratic equation:

$$\nu_T = \nu_0 + A T + B T^2 .$$

The results are reported in Table 1. In all cases the corresponding $^{65}$Cu NQR resonances were detected at a frequency of 0.925 times that of the corresponding $^{63}$Cu resonance.

Since the spins of both copper isotopes are 3/2, the unique resonance frequency is a function of both the coupling constant and the asymmetry parameter, $\eta$:

$$\nu_Q = \frac{e^2 Q q}{2} \sqrt{1 + \frac{\eta^2}{3}} .$$

It is only possible to separate $e^2 Q q$ and $\eta$ by Zeeman measurements on large ($\approx 1$ ml.) single crystals. The reactivity of these systems discouraged us from attempting the fabrication of such large crystals, so that the asymmetry parameters are unknown, but even for an asymmetry parameters as high as 0.5 the error in equating the coupling constant to twice the resonance frequency is only 4%.

Table 1. $^{63}$Cu NQR frequencies their temperature dependence.

| Complexes | $\nu_{77}$ (MHz) | $\nu_0$ (MHz) | $A$ (KHz K$^{-1}$) | $B$ (Hz K$^{-2}$) |
|---|---|---|---|---|
| **Ia** | 30.076 | 30.325 | −3.169 | −0.423 |
| | 30.003 | 30.256 | −3.332 | −0.193 |
| **Ib** | 30.273 [a] | 30.580 | −0.0851 | −10.391 |
| | 30.168 [b] | 30.280 | +1.580 | −13.460 |
| **Ic** | 30.229 | 31.475 | −10.812 | +17.751 |
| | 30.265 [c] | 30.436 | −0.8468 | −21.956 |
| | 30.023 [c] | 30.279 | −0.0995 | −11.083 |
| | 28.719 [d] | 29.829 | −3.076 | −6.254 |
| | 28.642 [d] | 29.983 | −4.258 | −2.661 |
| **IIa** | 33.683 | 34.847 | −2.316 | −14.437 |
| **IIb** | 35.588 | 36.037 | −4.494 | −9.741 |
| | 34.027 [e] | 37.418 | −1.312 | +6.231 |
| **IIc** | 35.081 | 35.736 | −7.729 | −4.164 |
| **III** | 31.306 [f] | 31.396 | −4.943 | −3.291 |
| | 31.889 [g] | 33.105 | 8.163 | −35.414 |

[a] At 164.9 K No signal below this temperature.
[b] At 171.3 K No signal below this temperature.
[c] At 147.1 K Phase change.
[d] At 243.1 K Phase change.
[e] At 320.5 K Phase change.
[f] At 187.2 K No signal below this temperature.
[g] At 217.3 K Phase change.

The resonance frequencies at 77 K for the two-coordinated siloxane complexes fall in a relatively narrow range between 28 – 32 MHz. The only previous measurement for an oxygen-coordinated compound of Cu(I) is that of $Cu_2O$ – probably the first Cu(I) compound studied by NQR – where each copper atom is also linearly bonded to two oxygen atoms, and the resonance frequency (26.697 MHz at 87 K, [3]) is noticeably lower than those reported here. In accord with the trend that was found for the two- or three-coordinated cations with pyridine ligands [4, 5] or the polyhalocuprate anions [6, 7], the resonance frequencies of the three-coordinated species are significantly higher than those of the two-coordinated complexes. The observation of two resonance frequencies for **Ia** and a single resonance frequency for **IIb** is in accord with their published crystal structures [2]. The temperature-dependence of the $^{63}$Cu resonances reveals that **Ib**, **Ic**, **IIb** and **III** undergo phase changes in the range 77 K – 300 K. This is illustrated for **Ic** in Fig. 1, where three distinct phases are present.

We have previously established, [8], that the $^{63}$Cu resonance frequencies of three-coordinated complexes $A_2CuB$ is influenced by the A-Cu-A bond-angle, $2\theta$. This behaviour could be explained on the basis of a partial field-gradient (pfg) model and it was shown that both the sense and the magnitude of the effect

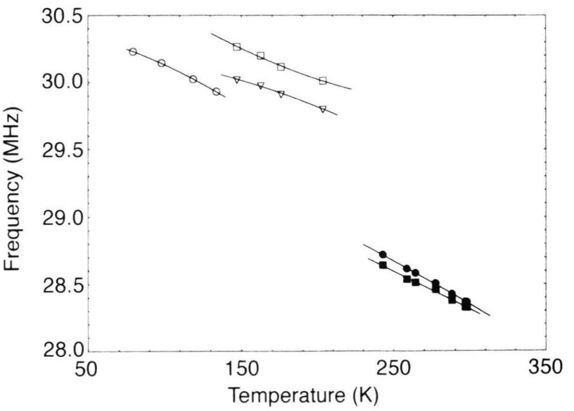


Fig. 1. The temperature dependence of the $^{63}$Cu resonance of **Ic** showing phase-changes.

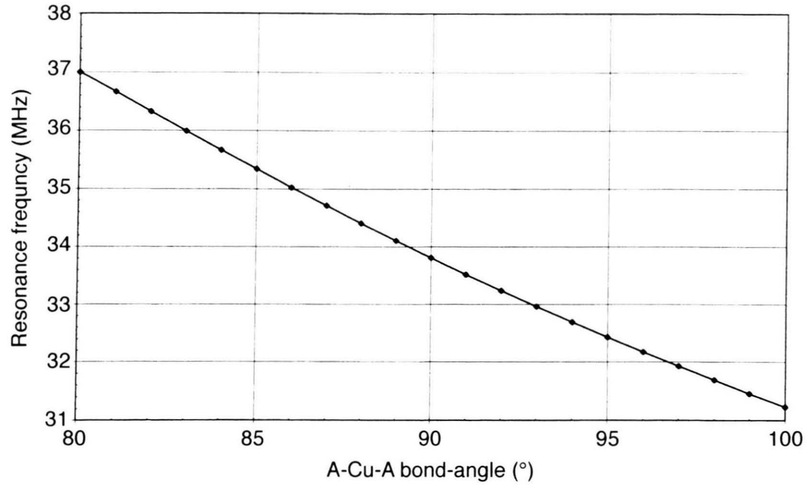
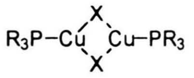


Fig. 2. The $^{63}$Cu resonance frequency predicted for a planar three-coordinated complex $A_2CuB$ by (1) for $e^2Qa = 18$ MHz and $e^2Qb = 21$ MHz as a function of the A–Cu–A angle.

depends on the difference between the partial field-gradients (a, b) of *A* and *B*, respectively:

$$\nu = e^2 Q \cdot \sqrt{(12a^2\cos^4\theta - (12a^2 - 6\alpha b)\cos^2\theta + 4a^2 - 2ab + b^2)}. \quad (1)$$

The frequencies of the three-coordinated species may be analysed with this equation, using the data for the analogous dimeric complex phosphine halides, **IV**, as reference compounds,



**IV**

The X–Cu–X bond-angle in the *tris*(o-tolyl)phosphineCuCl complex is 94.8° for a resonance frequency of 32.59 MHz, while in **IIb** the O–Cu–O angle is 84° for a by 3.0 MHz greater resonance frequency. It is, of course, impossible to obtain a set of partial coupling constants that reproduce the observed frequencies exactly, but an analysis of the results for various three-coordinated complexes that we have studied [1] implies values of 21–22 MHz for phosphines and thiones and 23 MHz, 21 MHz and 19 MHz for terminal chlorine, bromine and iodine, respectively. Bridging halides are, however, better represented by the lower values of 18, 16, and 15 MHz. With values such as these, (1) shows that the decrease in bond-angle for the siloxy complex would suffice to increase its frequency above that of the *tris*(o-tolyl)phosphine CuCl complex while retaining a partial coupling constant for the siloxy group equal to that of the chloride (Figure 2). Although oxygen is more electronegative than chlorine, and is thus expected to have a higher partial field-gradient, the electron-releasing silyl group would certainly suffice to reduce it to a value comparable to that of chlorine.

We have already established that it is not possible to carry over the partial coupling constant for ligands from three-coordinated to two-coordinated complexes. In all cases we have encountered that the partial coupling constants for three-coordinated species imply a frequency for the two-coordinated species that is in fact by 20%–30% higher than that observed. In accordance with this, in the present series the value of 18 MHz that we have just obtained for the three-coordinated species implies a frequency of 36 MHz, some 20% higher than the 28–32 MHz actually observed.

The crystal structures of the siloxane complexes other than **Ia** and **IIb** are unknown but the similarities between the frequencies in series **I** and **II** militate in favour of their having similar structures. Likewise, although there is no structure available for **III**, the fact that its resonance frequency is similar to that of **Ia** is a strong indication that it does indeed have a linear structure. The close similarity between its resonance frequency (31.306 MHz) and those of $[CuCl_2]^-$ anions (30.70 MHz and 31.15 MHz [6, 7, 9–11], is a further support of the above conclusion that the partial field gradient of the $R_3SiO^-$ group is very similar to that of $Cl^{-1}$.

## Conclusion

The $^{63}$Cu resonance frequencies of several three-coordinated Cu(I) complexes contained the $R_3SiO^-$ ligand show that the behaviour of this ligand is similar to that of $Cl^-$.

*Acknowledgements*

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