

⁶³Cu NQR Studies of Three-coordinated Complexes of Cu(I) with an Isocyanide Ligand*

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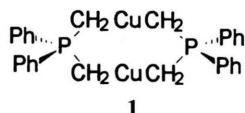
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Z. Naturforsch. **53a**, 599–602 (1998); received March 24, 1998

The ⁶³Cu NQR spectra of five three-coordinated complexes of Cu(I) containing an isocyanide ligand are reported. The resonance frequencies are compared with those of other three-coordinated Cu(I) complexes using a partial coupling constant model to describe the effects of the various ligands and to take into account the effects of variations in the molecular geometries. The partial coupling constant of the isocyanide ligand is much higher than that of any other ligand studied so far and leads to the order of donor atom partial field gradients for terminal ligands C>N>Cl>P≈S≈Br>I>O.

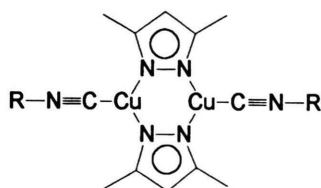
Introduction

Whereas we have extensively reported the ⁶³Cu NQR spectra of complexes of Cu(I) with ligands having nitrogen, sulphur, phosphorus, chlorine, bromine and iodine as the donor atom [1–4], we have only been able to observe resonances from one class of complexes with a ligand, the siloxyl group, having oxygen as donor [5], and until now have been unsuccessful in observing resonances from ligands with a carbon atom as donor. We may mention in this context our failure with the two-coordinated anionic complexes [PhCuPH][Li(12-crown-4)₂] and [MeCuMe][Li(12-crown-4)₂] and with the neutral ylide **1**, [Ph₂P(CH₂)₂Cu]₂.



To our knowledge the only report of resonances from an organocopper complex concerns three aryl copper complexes with two- or three-coordinated copper atoms [6].

We now report resonances from the following complexes containing an isocyanide group as one of the ligands:



I. R = cyclohexyl; II. R = t-butyl; III. R = 2, 6 dimethylphenyl; IV. R = 4-chlorophenyl; V. R = phenyl.

Experimental

Preparations

Pyrazole, 3,5-dimethylpyrazole, cyclohexyl isocyanide, t-butyl isocyanide, 2,6-diphenyl isocyanide and benzyl isocyanide were commercially available (Aldrich). Phenyl isocyanide and 4-chlorophenyl isocyanide were prepared by literature methods [7, 8]. The complexes were prepared according to the literature method [9]. All preparations were carried out under strictly anhydrous and anaerobic conditions under an atmosphere of nitrogen.

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

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

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Results and Discussion

NQR

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

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

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 η :

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

It is only possible to separate $e^2 Qq$ and η by Zeeman measurements on large (≈ 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 parameter as high as 0.5, the error in equating the coupling constant to twice the resonance frequency is only 4%.

In accord with its reported crystal structure [9] there is only one resonance for **I**, whose frequency has the usu-

Table 1. ^{63}Cu NQR frequencies of Cu(I) isocyanide complexes and their temperature dependence.

Complexes	ν_{77} (MHz)	ν^0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)
I	41.841	42.165	−2.765	−12.525
II	43.712 ^a	44.756	−4.860	−17.385
	44.071 ^b	44.350	−0.729	−35.000
	44.259 ^c	44.194	−5.416	−8.323
	43.029 ^d	44.520	−7.364	−6.821
III	40.043	40.847 ^e	−1.958	−17.577
	38.997 ^f	46.261	−3.931	+50.144
IV	41.452 ^g			
V	39.241 ^h	39.028	+13.915	−45.147
	38.952 ^h	33.592	+4.992	−101.767

^a 77–170 K. ^b 77–142.5 K. ^c 77–170 K. ^d At 175.3. Temperature dependence studied until 312 K. ^e 77–290 K. ^f At 298 K. Temperature dependence studied until 312 K. ^g At 293 K. No signal detected at lower temperatures. ^h At 293 K. Temperature dependence studied until 314 K. No signal detected at lower temperatures.

al negative temperature dependence and which is observable over the entire range of 77–300 K. **II** shows three closely-spaced resonances in the range 77–180 K but above this temperature only one resonance is present, indicative of a phase-change (Figure 1). For **III** there is again a phase-change, at 285 K, but only one resonance is present in both phases, while no resonance could be

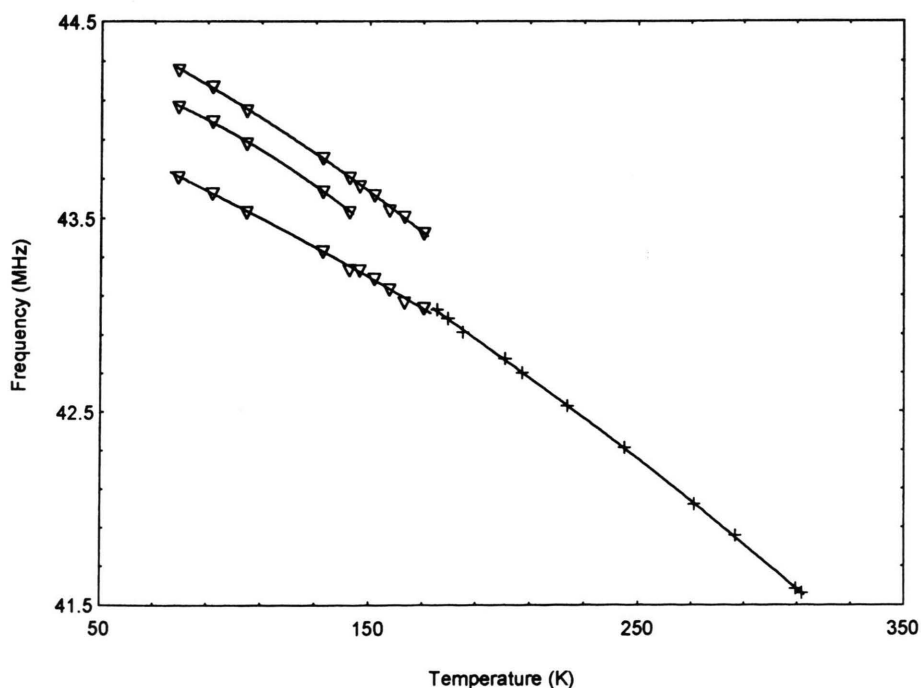


Fig. 1. Temperature dependence of the ^{63}Cu NQR frequencies of **II**.

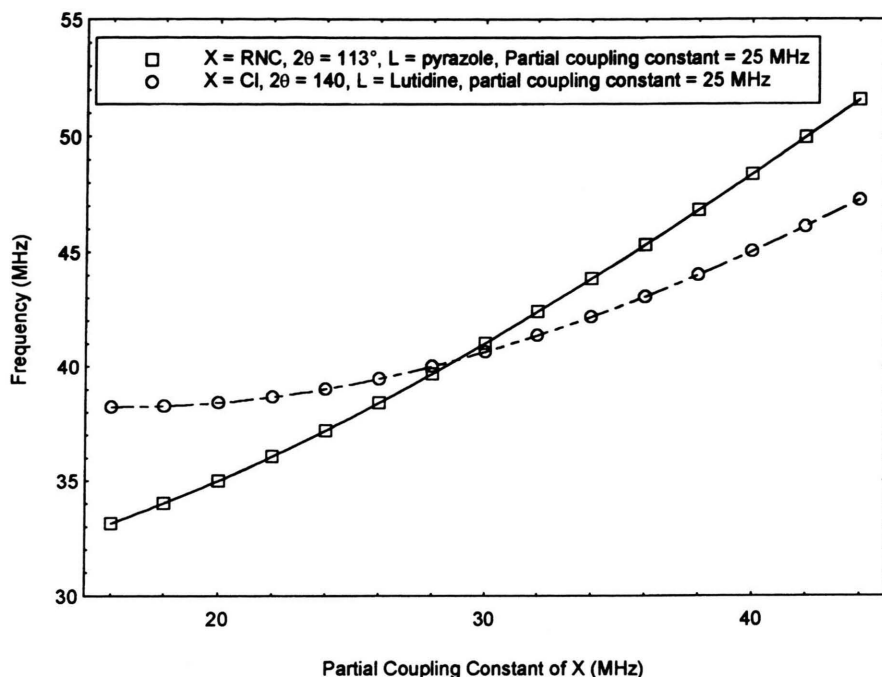


Fig. 2. Predicted ^{63}Cu NQR frequency of A_2CuB as a function of the partial coupling constant of B for A=lutidine and A=pyrazole.

observed below 168 K. **IV** showed only a single resonance of low intensity at 293 K, and no signal could be detected below this temperature. Finally, **V** shows two resonances from 293 to 314 K, the upper limit of our study of its temperature-dependence, but no signal could be observed in the range 77–293 K.

The resonance frequencies at 77 K for these complexes fall in a rather large range, 44 MHz for **II** and 40 MHz for **III**. The frequencies may be compared with those of the *bis*(2,6-lutidine)cuprous halides; 38.35, 37.61, and 35.30 for X=Cl, Br and I, respectively, while a second crystalline form of the iodide has a resonance frequency of 36.96 MHz, [10]. They thus appear to conform to the general trend that for a given type of complex the more electronegative or the harder the donor atom, the higher the resonance frequency, e.g. $\text{Cl} > \text{Br} > \text{I}$ and $\text{N} > \text{P}$.

We have previously established [3], that the ^{63}Cu resonance frequencies of the three-coordinated complexes A_2CuB are influenced by the A-Cu-A bond angle, 2θ . This behavior could be rationalized on the basis of a partial field-gradient model, and it was shown that both the sense and magnitude of the effect depends on the difference between the partial field-gradients, q_a and q_b , of A and B respectively, according to the equation

The bond-angles in the lutidine complexes are quite large, ranging from 139.7° for the chloride to 149.6° for the higher frequency modification of the iodide, whereas in **I** the bond-angle is 113° . Appropriate values of the partial coupling constants, eQq_a and eQq_b , for the lutidine and chlorine ligands in these neutral three-coordinated complexes are 25 MHz and 23 MHz, respectively. Our studies of two-coordinated lutidine, imidazole and pyrazole cations, [1, 4], shows that, despite the shorter Cu bond-length in the imidazole and pyrazole complexes compared to the lutidine complexes, the partial coupling constants of all three ligands are very similar. Figure 2 shows the predictions of (1) for the dependence of the resonance frequency of a complex A_2CuB on e^2Qq_b , where e^2Qq_a is taken to be 25 MHz, $2\theta = 140^\circ$ for the lutidine complex chloride and 113° for **I**. This shows that, whereas the resonance frequency of the lutidine complexes is not very dependent on e^2Qq_b , the frequency of 41 MHz for **I**, where 2θ is only 113° , implies that $e^2Qq_{\text{isocyanide}}$ must be much higher than e^2Qq_{lutidine} , around 31 MHz. Equation (1) also offers a possible explanation of the range in resonance frequencies of the isocyanide complexes in that with eQq_a and eQq_b , taken as 25 and 31 MHz, respectively, a bond angle of 113°

$$\nu = e^2Q\sqrt{(12q_a^2\cos^4\theta - (12q_a^2 - 6q_aq_b)\cos^2\theta - 4q_a^2 - 2q_aq_b + q_b^2)}. \quad (1)$$

implies a resonance frequency of 41.7 MHz, whereas an increase to 120° causes a drop to 40.8 MHz, and a decrease to 106° increases it to 43.2 MHz.

Conclusion

The partial coupling constants of the isocyanide ligand, 31 MHz, is much higher than that of any other

ligand studied so far and leads to the order of donor atom partial field gradients for terminal ligands $\text{C} > \text{N} > \text{Cl} > \text{P} \approx \text{S} \approx \text{Br} > \text{I} > \text{O}$.

Acknowledgements

We thank the Swiss National Research Fund for their support

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