^{63,65}Cu and ^{79,81}Br NQR Studies of Thione Complexes of Cu(I) Halides*

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^{63,65}Cu NQR frequencies, together with their temperature dependence, are reported for several complexes formed between cuprous chloride or bromide and heterocyclic thiones. For bromides the ^{79,81}Br resonances have also been detected. These results indicate that, with one exception, the copper atom is tricoordinated by two sulphur atoms and one halogen. Several of these complexes show phase changes in the range 77–300 K.

Key words: NQR, Copper(I), Thione.

Introduction

The complexes of monovalent copper are notorious for the variability of their structures [1]. Although the copper atom will adopt, if posssible, a tetrahedral coordination, should factors such as stereochemistry or total charge intervene, coordination numbers of three (trigonal) or two (linear) are commonplace. This, combined with a readiness to form polynuclear complexes with bridging ligands, leads to an extreme variability in the structure of such complexes, so that their molecular formulae are by no means a reliable indication of their molecular structure.

Cu(I) forms its most stable complexes with "soft" ligands such as sulphur and phosphorous, and the complexes of cuprous halides with sulphur-containing ligands were the first to yield ^{63,65}Cu NQR frequencies [2, 3]. A certain body of experimental NQR data, combined with a few crystal-stuctures thus make these complexes good candidates for the identification of their structure using NQR spectroscopy, and we report here the results for a number of complexes with heterocyclic thiones.

Experimental

Preparations

The ligands, except for thiocaprolactam and thiazolidine-2-thione, which were commercially available (Aldrich, Fluka), were prepared according to the methods reported in [4]. The complexes were all prepared by previously-described methods [5–8]. To remove any doubt as to the identity of the 1:1 and 2:1 complexes, Cu(thiocaprolactam)Br and Cu(thiocaprolactam)$_2$Br, we obtained their elemental analyses**.

(1:1) C = 27.15% (26.43%), H = 4.11% (4.07%), N = 5.27% (5.14%);

(2:1) C = 35.81% (35.86%), H = 5.40% (5.52%), N = 7.06% (6.97%).

The theoretical values are shown in parentheses.

NQR

NQR spectra were measured on a Decca superregenerative spectrometer, frequences 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

Resonance Frequencies

The ligands, thiocaprolactam, I, N-alkyl imidazolidine-2-thiones, II, and thiazolidine-2-thione, III, used in this study are shown below, while the resonance frequencies of the complexes are shown in Tables 1 and 2. For ^{63}Cu the complete temperature dependence of the resonance frequencies was observed and

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Table 1. The frequencies and temperature dependence of the ^{63}Cu NQR spectra of complexes of cuprous chloride and bromide with heterocyclic thiones. In all cases the corresponding ^{65}Cu resonances were also observed at a frequency of 0.925 times that of the ^{63}Cu isotope.

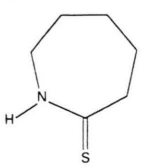
Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K^{-1})	B (Hz K^{-2})
Cu(1,3-thiazolidine-2-thione)$_2$Cl	27.400	27.596	−1.882	−6.507
Cu(1,3-thiazolidine-2-thione)$_2$Br	27.059	27.161	−0.528	−8.234
Cu(thiocaprolactam)Cl	32.373	32.763	−4.367	−7.438
Cu(thiocaprolactam)Br	31.699	32.095	−4.423	−7.590
Cu(thiocaprolactam)$_2$Br	30.879	31.248	−4.436	−3.200
Cu(N-methylimidazolidine-2-thione)$_2$Cl	30.768	31.363	−8.177	6.097
Cu(N-methylimidazolidine-2-thione)$_2$Br	29.324	29.526	−2.004	−5.737
Cu(N-ethylimidazolidine-2-thione)$_2$Cl	30.296 30.161	30.748[a]	−4.609	−6.480
Cu(N-ethylimidazolidine-2-thione)$_2$Br	29.393	29.539[b]	−0.487	−18.429
Cu(N-propylimidazolidine-2-thione)$_2$Cl	30.046	29.939[c]	3.770	−30.457
		30.706[d]	−6.210	−1.906
	29.295	29.688[e]	−4.703	−2.852
		29.633[d]	−5.381	0.955
Cu(N-propylimidazolidine-2-thione)$_2$Br	28.893	29.233	−3.611	−7.359
Cu(N-isopropylimidazolidine-2-thione)$_2$Cl	32.722[f]	33.293[g]	−4.547	−11.164
Cu(N-isopropylimidazolidine-2-thione)$_2$Br	30.343	30.953	−7.668	0.291

[a] For the temperature range 104–300 K.
[b] For the temperature range 77–237 K.
[c] For the temperature range 77–192 K.
[d] For the temperature range 232–303 K.
[e] For the temperature range 77–230 K.
[f] Measured at 100 K; the resonances are undetectable at 77 K.
[g] For the temperature range 100–310 K.

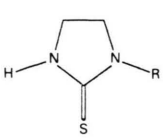
the results fitted to the quadratic equation

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

The coefficients of this equation are shown in Table 1. For the $^{79,81}Br$ nuclei only measurements at 77 K and 298 K are reported, except for Cu(N-ethylimidazolidine-2-thione)$_2$Br and Cu(1,3-thiazolidine-2-thione)$_3$Br, where phase changes occur and for which we report the above coefficients determined over part of the temperature range.



(I)



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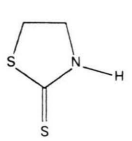

(III)

Table 2. ^{79}Br and ^{81}Br resonance frequencies of complexes of cuprous bromide with heterocyclic thiones.

Complex	ν_Q ^{79}Br (MHz)		ν_Q ^{81}Br (MHz)	
	77 K	298 K	77 K	298 K
Cu(1,3-thiazolidine-2-thione)$_2$Br	44.491	43.281	37.161	36.177
Cu(1,3-thiazolidine-2-thione)$_3$Br	30.909 30.073	30.093[a]	25.832 25.133	25.149
Cu(thiocaprolactam)Br	48.058	47.106	40.165	39.354
Cu(thiocaprolactam)$_2$Br	50.831	49.390	42.482	41.273
Cu(N-methylimidazolidine-2-thione)$_2$Br	51.27	48.93	42.85	40.87
Cu(N-ethylimidazolidine-2-thione)$_2$Br	48.11	45.74	40.18[b]	38.25
Cu(N-propylimidazolidine-2-thione)$_2$Br	–	48.98	–	40.91
Cu(N-isopropylimidazolidine-2-thione)$_2$Br	49.99	48.38	41.77	40.92

[a] The temperature-dependence of ^{79}Br was determined in the range 147–308 K and yielded the results $\nu_0 = 29.454$ MHz, $A = 1.123$ kHz K^{-1}, $B = 3.544$ Hz K^{-2}.
[b] The temperature-dependence of ^{81}Br was determined in the range 77–230 K and yielded the results $\nu_0 = 40.637$ MHz, $A = -5.05$ kHz K^{-1}, $B = -11.35$ Hz K^{-2}.

All four nuclei studied here have spins $I = 3/2$ so that the resonance frequencies are related to the coupling constant, e^2Qq_{zz}, and the asymmetry parameter, η, by the equation

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

where the asymmetry parameter is defined as

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}.$$

It is only possible to separate the two terms in this equation by means of Zeeman measurements on large single crystals, and attempts to grow such crystals are currently under way. However, even for an asymmetry parameter as large as 0.5, its effect on the resonance frequency is negligible compared to that of the coupling constant itself.

Previous studies of complexes with sulphur-containing ligands [2, 3, 9] indicate that for such complexes with tricoordinated copper atoms the ^{63}Cu frequencies would lie in the neighbourhood of 30 MHz. The crystal structure of Cu(N-ethylimidazolidine-2-thione)$_2$Cl shows it to be a monomer [10]. Only one chemically distinct molecule is present and, in accordance with this, there is only one resonance at room-temperature, but at 104 K a phase-transition occurs (Fig. 3) and the two lines reported in the Table appear.

All previous studies of ^{63}Cu frequencies of complexes of cuprous halides indicate that, for the same ligand, corresponding complexes of the cuprous halides have frequencies in the order Cl > Br > I. Thus the fact that the frequency of Cu(N-ethylimidazolidine-2-thione)$_2$Br is approximately 1.0 MHz lower than that of the chloride is consistent with the hypothesis that it, too, has a trigonal planar structure. Furthermore, inasmuch as the frequencies of the methyl and propyl derivatives are similar to those of the ethyl derivatives, it seems likely that they, also, are trigonal planar monomers. The complexes formed by isopropylimidazolidine-2-thione and thiazolidine-2-thione present, however, a difficulty since, although on the basis of their empirical formula one is likewise tempted to assign a trigonal planar structure to them, their ^{63}Cu NQR frequencies are, respectively higher and noticeably lower than those of the complexes with N-ethylimidazolidine-2-thione. The same remark applies to Cu(thiocaprolactam)$_2$Br. It is possible that these differences are associated with changes in the Cu–S bond-lengths or with the bond-angles brought about by differences in the steric hindrance of the ligands [11].

The two 1:1 complexes with thiocaprolactam are, no doubt, dimers. The ^{63}Cu NQR frequencies do not, however, permit a choice to be made between halogen bridges or sulphur bridges. The ^{79}Br frequency militates, however, in favour of a sulphur bridge since, on the one hand it is quite similar to that of Cu(N-ethylimidazolidine-2-thione)$_2$Br and the other three-coordinated bromides, and on the other, our studies of bridged binuclear cuprous polyhalide anions [12] revealed that in these complexes bridging bromine atoms have frequencies greater than 60 MHz. The fact that the chloride has a ^{63}Cu NQR frequency higher than that of the bromide is evidence that these two complexes have similar structures.

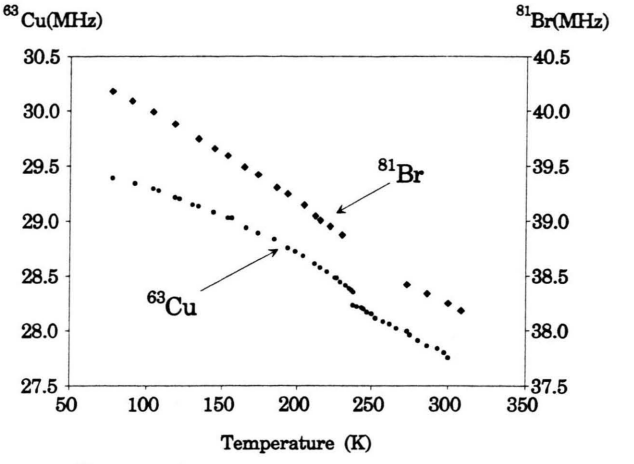

Fig. 1. ^{63}Cu and ^{81}Br NQR temperature dependences for Cu(ethylimidazolidine-2-thione)$_2$Br.

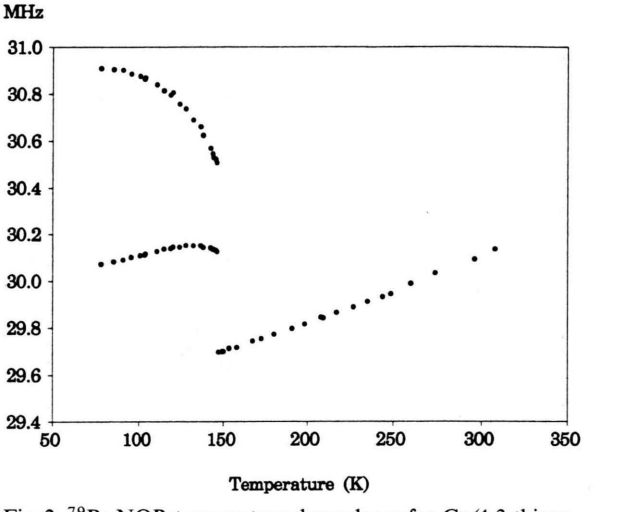

Fig. 2. ^{79}Br NQR temperature dependence for Cu(1,3-thiazolidine-2-thione)$_3$Br.

Temperature Dependence and Phase Changes

A number of these complexes exhibit phase-changes in the temperature range 77–300 K. The complete temperature dependence for such cmplexes is shown in Figures 1–4. Figure 1 shows the temperature dependence of both ^{63}Cu and ^{81}Br for Cu(ethylimidazolidine-2-thione)$_2$Br. The ^{63}Cu resonance broadens and decreases in intensity as the temperature is raised from 77 K, and at 238 K there is an abrupt frequency shift. Further increase in temperature results in an increase in intensity accompanied by the usual decrease in frequency. A similar behaviour occurs for the ^{81}Br resonance but, owing to the poor signal-to-noise ratio of this resonance, the signal was undetectable in the region of the phase change. Figure 2 shows the temperature dependence for the ^{79}Br in Cu(1,3-thiazolidine-2-thione)$_3$Br, where below the transition temperature of 146 K there are two distinct bromine atoms in the unit cell but only one above it. Furthermore, in the high temperature phase the bromine resonance exhibits an anomalous positive temperature

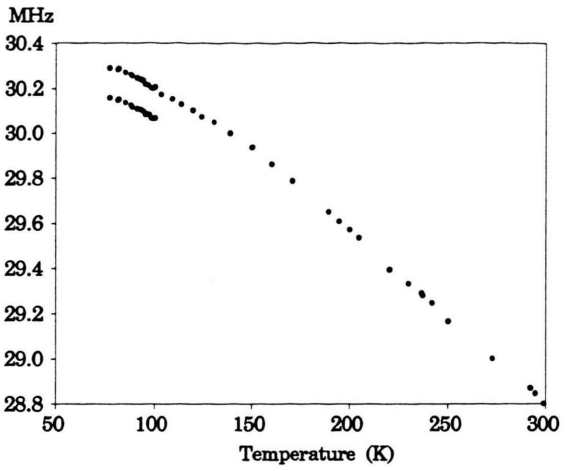

Fig. 3. ^{63}Cu NQR temperature dependence for Cu(ethylimidazolidine-2-thione)$_2$Cl.

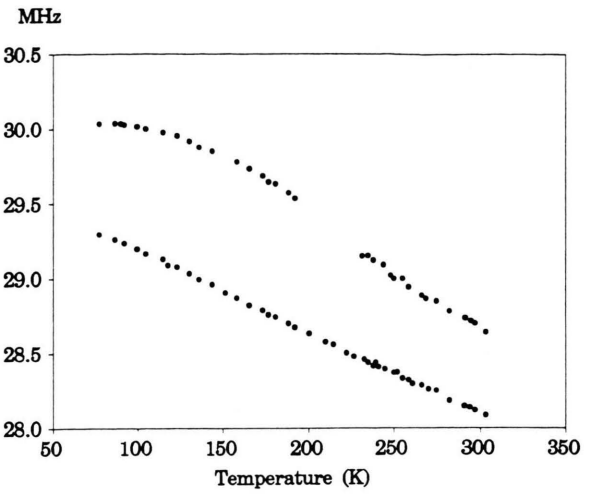

Fig. 4. ^{63}Cu NQR temperature dependence for Cu(propylimidazolidine-2-thione)$_2$Cl.

coefficient. We were unable to detect any resonances from the copper nuclei; they probably lie below the 12 MHz lower limit of our spectrometer. Figure 3 gives the results for the ^{63}Cu resonances of Cu(ethylimidazolidine-2-thione)$_2$Cl, which shows a phase change at 104 K where the number of distinct copper atoms passes from two, in the low-temperature range, to one, above the transition temperature. Finally, the temperature-dependence of the copper resonances in Cu(propylimidazolidine-2-thione)$_2$Cl, Fig. 4, is curious in that, whereas the resonance at the lower frequency evolves apparently continuously throughout the whole range, that at higher frequency fades out in the range 192–231 K.

Conclusion

Although the ^{63}Cu NQR frequencies support a trigonal planar structure for the complexes discussed here, it will be necessary to determine a few more crystal structures of these thione complexes of Cu(I) halides so as to cast light on the variations in the resonance frequencies of apparently structurally similar complexes.

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