Nuclear Quadrupole Resonance Spectra of Pyridine *N*-Oxide Complexes of Copper(II) Halides

By J. J. R. Fraústo da Silva* and R. Wootton

[*Centro de Estudos de Química Nuclear* (*I.A.C.*), *Instituto Superior Técnico, Lisboa, Portugal*]

Summary The pure n.q.r. resonance spectra of ^{35}Cl and ^{79}Br in cupric chloride and bromide complexes of pyridine *N*-oxide are used to obtain structural information.

The crystal structure of $CuCl_2$(pyridine *N*-oxide) grown as needle crystals from ethanol solution has been reported to be a pyridine *N*-oxide bridged dimer;[1] the two chlorine atoms bonded to each copper were thought to be both terminal. In a later paper, the structure was described more accurately as consisting of oxygen-bridged dimers held together in infinite chains by chlorine bridges.[2] One of the chlorine atoms is terminal and the other interacts rather weakly with a second copper atom (bond distance 2·803 Å, as compared with 2·206 Å for the "normal" bond). These differences should be noticeable in their respective n.q.r. frequencies, but we were unable to detect any signals from crystals grown in this way, presumably due to crystal imperfections; however, slow evaporation of a hot (*ca.* 70°) aqueous solution of the complex resulted in green, rectangular plates which at room temperature gave two signals of approximately equal intensity for each chlorine isotope (see Table), indicating that there are two nonequivalent chlorine atoms in these crystals also.

This is one of the first studies of complexes of copper(II) using n.q.r.; the interpretation of the results must suffer from the lack of systems for comparison. However, the quadrupole resonance frequency of ^{35}Cl in hydrated cupric chloride, which contains only bridging chlorine atoms,[3] has been determined as 9·01 MHz at room temperature.[4] In contrast, the resonance frequencies for the 1 : 1 pyridine *N*-oxide complex are much higher, and the ratio of these to that of cupric chloride is of the general order found for the terminal to bridging ratio of other compounds.[5] The separation between the two signals of approximately 0·3 MHz is small, but larger than has generally been found to result from crystallographically nonequivalent sites for chemically equivalent nuclei in this low frequency range.[5] The result of two resonances, therefore, supports the reported crystal structure[2] and suggests that the geometry about the copper in needle and plate crystals is the same. In fact, the plates appear to contain one molecule of water per dimeric unit (thermogravimetric analysis), but the i.r.

Table[a]

Compound	Resonance frequency of ^{35}Cl or ^{79}Br at room temperature (293°K) (MHz)	Approximate signal to noise ratio
$CuCl_2,2H_2O$	9·01[b]	70
$CuBr_2$	83·5	
$CuCl_2$(pyridine *N*-oxide) ..	11·80	10
	12·08	10
$CuBr_2$(pyridine *N*-oxide) ..	109·5	30
	114·2	35
$CuCl_2$(pyridine *N*-oxide)$_2$ ..	11·56	8
	12·48	9

[a] Data obtained on a Wilks model N.Q.R. 1A spectrometer with 1 g samples and time-constant 30 sec. Frequencies for Cl and Br resonances are reliable to ± 0·01 and ±0·1 MHz respectively, due to the combination of measuring instrument error and uncertainty in assigning fundamental bands.

[b] Data from ref. 4.

stretching frequencies of this water at *ca*. 3540 and 3475 cm^{-1} indicate that it is not involved in co-ordination.

$CuBr_2$(pyridine *N*-oxide) when crystallised from hot water gave dark-brown, rectangular plates, which were anhydrous. These also had two resonance frequencies of approximately equal intensity for each bromine isotope, at room temperature. This provides good evidence for a similarly distorted square pyramidal geometry about the copper atoms in their complex. The resonance frequency for cupric bromide was also determined and, as for the chloride case, was much lower than the frequencies for its 1 : 1 pyridine *N*-oxide; cupric bromide is known to contain only bridging bromine atoms.[6]

The 2 : 1 complexes, CuX_2(pyridine *N*-oxide)$_2$ crystallised from hot water were also studied. No signals could be detected for the light-brown bromide complex, but the olive-green chloride complex gave two signals, both shifted from the positions in the 1 : 1 complex, one to higher and one to lower frequency. The exact reasons for these shifts cannot readily be appreciated at present, but they imply a more pronounced nonequivalency of the two chlorine atoms.

One of us (R.W.) acknowledges a grant under the programme of the 3rd Development Plan—Fomento da Acção Educativa of the Ministério de Educação Nacional (Portugal).

(*Received, November 28th*, 1969; *Com*. 1819.)

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