63Cu NQR spectra of dicoordinated Cu(I) cations with imidazole and pyrazole ligands

KHAJEHNOURI, Fereidoun, MOTALLEBI, Shahrokh, LUCKEN, Edwin-Anthony

Abstract
The 63Cu NQR spectra of five dicoordinated complex cations of Cu(I) with substituted imidazoles as ligands and six analogous complexes with substituted pyrazoles as ligands are reported. The structures of four of these complexes have been previously determined and the relationship of their 63Cu resonance frequency to the average Cu---N bond length is compared to that of the analogous lutidine or collidine complexes. It is concluded that there are probably significant differences between the electronic structures of the pyridine complexes and those of the pyrazole or imidazole series.

Reference

DOI : 10.1016/0022-2860(94)08479-2
**Abstract**

The $^{63}$Cu NQR spectra of five dicoordinated complex cations of Cu(I) with substituted imidazoles as ligands and six analogous complexes with substituted pyrazoles as ligands are reported. The structures of four of these complexes have been previously determined and the relationship of their $^{63}$Cu resonance frequency to the average Cu–N bond length is compared to that of the analogous lutidine or collidine complexes. It is concluded that there are probably significant differences between the electronic structures of the pyridine complexes and those of the pyrazole or imidazole series.

1. **Introduction**

Whereas the dicoordinated complex cations of copper(I) with substituted pyridine ligands are, in the solid state, relatively stable towards atmospheric oxygen, the corresponding complexes with the sp$^2$ donor nitrogen atom forming part of a five-membered ring such as pyrazole or imidazole are rapidly oxidized. Thus the pyridine complexes can be prepared with the simplest of precautions to avoid the presence of an oxidizing agent in the reaction solution and the dry solid product can be manipulated in the open laboratory with impunity, while the imidazole and pyrazole complexes must be prepared and the solid product handled under rigorously anaerobic conditions.

Another difference between these two series of complexes is that the N–Cu bond lengths (1.85–1.88 Å) in the pyrazole and imidazole complexes [1–3] are significantly less than those (1.90–1.94 Å) of the analogous pyridine complexes [4–7]. For the pyridine series, where a necessary condition for the formation of a dicoordinated species is that both ortho positions carry substituents, the Cu–N bond length can be varied to some extent by the relative orientation of the pyridine rings that modifies the steric interactions between these substituents, we have shown that there is a good correlation between the $^{63}$Cu NQR frequency and the Cu–N bond length [7]. If this correlation were to persist in the imidazole and pyrazole series, where there are no substituents adjacent to the coordinating nitrogen atom, then it would indicate that the shorter bond length can be ascribed to a decreased steric hindrance and that the marked difference in reactivity between the two series of complexes may not be due to any fundamental difference between the metal–ligand bonding in these two series of complexes but be only a...
consequence of the closer interaction between the ligand and the metal atom. If the correlation is markedly different, however, it would indicate that the nature of the bonding is significantly different in the two series.

We have therefore prepared the following eleven imidazole or pyrazole complexes, \([L_2Cu]^+X^-\), including all those for which structural data are available, and report their $^{63}$Cu NQR spectra: 1, \(L = 1\)-methylimidazole, \(X = BF_4^-\); 2, \(L = 2\)-methylimidazole, \(X = BF_4^-\); 3, \(L = 1,2\)-dimethylimidazole, \(X = PF_6^-\); 4, \(L = 1,2\)-dimethylimidazole, \(X = BF_4^-\); 5, \(L = 2\)-ethylimidazole, \(X = BF_4^-\); 6, \(L = 4\)-methylpyrazole, \(X = BF_4^-\); 7, \(L = 2\)-methylpyrazole, \(X = BF_4^-\); 8, \(L = 3,5\)-dimethylpyrazole, \(X = BF_4^-\); 9, \(L = 1,3,5\)-trimethylpyrazole, \(X = BF_4^-\); 10, \(L = 1\)-ethylpyrazole, \(X = BF_4^-\); 11, \(L = 1\)-ethylpyrazole, \(X = PF_6^-\).

### Table 1

$^{63}$Cu NQR resonances in the temperature range 77–300 K and the results fitted to the equation \(\nu_T = \nu_0 + AT + BT^2\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_{RT}) (MHz)</th>
<th>(\nu_{RT'}) (MHz)</th>
<th>(\nu_0) (MHz)</th>
<th>(A) (kHz K(^{-1}))</th>
<th>(B) (Hz K(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.884</td>
<td>40.886</td>
<td>41.205</td>
<td>-3.564</td>
<td>-2.843</td>
</tr>
<tr>
<td>2</td>
<td>40.723</td>
<td>41.913</td>
<td>42.080</td>
<td>-1.143</td>
<td>-10.636</td>
</tr>
<tr>
<td>3</td>
<td>40.667</td>
<td>41.578</td>
<td>41.792(^a)</td>
<td>-2.438(^a)</td>
<td>-2.830(^a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41.812(^b)</td>
<td>-0.546(^b)</td>
<td>-10.657(^b)</td>
</tr>
<tr>
<td>4</td>
<td>40.603</td>
<td>41.161</td>
<td>41.116(^c)</td>
<td>0.735(^c)</td>
<td>-10.098(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40.793(^d)</td>
<td>4.315(^d)</td>
<td>-16.497(^d)</td>
</tr>
<tr>
<td>5</td>
<td>40.794</td>
<td>41.882</td>
<td>42.220</td>
<td>-3.302</td>
<td>-5.031</td>
</tr>
<tr>
<td>6</td>
<td>38.478</td>
<td>40.121</td>
<td>40.676</td>
<td>-6.106</td>
<td>-4.370</td>
</tr>
<tr>
<td>7</td>
<td>37.973</td>
<td>39.968</td>
<td>40.446</td>
<td>-4.981</td>
<td>-1.090</td>
</tr>
<tr>
<td>8</td>
<td>39.984</td>
<td>40.925</td>
<td>41.189(^e)</td>
<td>-1.539(^e)</td>
<td>-20.227(^e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>41.532(^f)</td>
<td>-3.833(^f)</td>
<td>-4.330(^f)</td>
</tr>
<tr>
<td>9</td>
<td>40.924</td>
<td>42.536</td>
<td>42.740(^g)</td>
<td>-2.225(^g)</td>
<td>-4.159(^g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42.093(^h)</td>
<td>-2.525(^h)</td>
<td>-4.063(^h)</td>
</tr>
<tr>
<td>10</td>
<td>39.243</td>
<td>40.381</td>
<td>40.397</td>
<td>0.926</td>
<td>-16.238</td>
</tr>
<tr>
<td>11</td>
<td>39.115</td>
<td>39.667</td>
<td>39.715</td>
<td>-0.0923</td>
<td>-6.221</td>
</tr>
</tbody>
</table>

\(^a\) Low temperature phase, 77–161 K.
\(^b\) High temperature phase, 161–300 K.
\(^c\) Low temperature phase, 77–140 K.
\(^d\) High temperature phase, 140–300 K.
\(^e\) Low temperature phase, 77–140 K.
\(^f\) High temperature phase, 77–140 K.
\(^g\) Low temperature phase, 140–300 K.
\(^h\) Low temperature phase, 77–130 K.

### 2. Experimental

#### 2.1. Preparations

The complexes were prepared under dry dinitrogen according to the published method [1]. Solvents were distilled under dinitrogen after previous drying over an appropriate reagent (methanol over magnesium methoxide, acetonitrile and dimethylformamide over calcium hydride, tetrahydrofuran and diethyl ether over sodium). The ligands were either commercially available (Aldrich) or prepared according to a published method [8]. For the NQR measurements the dry crystalline products were transferred in a dry-box to glass vials of 10 mm diameter and sealed under dinitrogen.

#### 2.2. NQR

NQR spectra were measured on a Decca superregenerative spectrometer 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.

### 3. Results and discussion

#### 3.1. NQR

The $^{63}$Cu NQR spectra and their temperature dependence were observed in the range 77–300 K and the results fitted to a 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 observed at a frequency of 0.925 times that of the corresponding $^{63}$Cu resonance. In all cases only one $^{63}$Cu resonance was observed, thus showing, in agreement with the published crystal structures of 1, 3, 6 and 9 [1–3], that there is only one distinct copper cation present in the unit cell. A phase change, as evidenced by a discontinuity in the temperature dependence of the $^{63}$Cu frequency, occurs for 3 at 160 K, for 4 at 140 K, for 8 at 140 K and for 9 at 130 K. A typical example of such discontinuities
is shown in Fig. 1 for 3. In no case is there any change in the multiplicity of the NQR signal.

Since the spins of both copper isotopes are $\frac{3}{2}$ 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 parameter as high as 0.5 the error in equating the coupling constant to twice the resonance frequency is only 4%.

The eleven complexes have room temperature resonance frequencies that fall in the range 38–41 MHz. Only 1, 3, 6 and 9 are of known structure [1–3], all with an almost linear N–Cu–N geometry, with two almost coplanar five-membered rings and with two slightly different Cu–N bond lengths falling in the range 1.879–1.855. The frequencies of the analogous pyridine complexes fall in the range 39.1–41.9 MHz and the correlation equation [7] between the NQR frequency at room temperature, $\nu_{RT}$, and the bond length $R_{CuN}$ is given by

$$\nu_{RT} = 157.66 - 61.136 R_{CuN}$$

This equation applied to 1, 3, 6 and 9 predicts resonance frequencies of 44.0, 43.6, 43.0 and 43.5 MHz respectively, differing by 4.0, 4.1, 4.5 and 2.6 MHz from the observed frequencies. On the other hand the seven frequencies of the pyridine complexes fit the above equation with a maximum deviation of 0.33 MHz. Fig. 2 shows the data for the two series of complexes and shows that the four points for the five-membered ring ligands do not appear to be well correlated but fall very roughly on a line parallel to that for the pyridine series but shifted from it by about 3 MHz. We may thus safely conclude that there are essential
differences between the imidazole or pyrazole complexes and the pyridine complexes.

The question remains, however, as to whether the reason for this difference resides in the structure of the isolated cation or in an effect arising from some detail of the crystal structure. Thus for the pyridine complexes the crystal structure [5] of (2,6-lutidine)$_2$CuNO$_3$ indicates that the nitrate anion is weakly coordinated to the Cu(I) cation and this increase in the coordination number of the metal ion reveals itself in a sharp drop in the resonance frequency to 32.650 MHz from the value of 41.275 MHz for the corresponding tetrafluoroborate [9]. A similar frequency lowering was observed [9] for other (2,6-lutidine)$_2$Cu$^+$ species with soft counter-anions such as CF$_3$CO$_2$. The crystal structure [2] of 1 reveals that while one of the fluorine atoms of the BF$_4^-$ anion is at a distance of 3.474 Å the other three distances lie in the range 4.47–5.57 Å but for 6 and 9 the shortest Cu–F distance is more than 5 Å. This is certainly not indicative of any significant coordination between the anion and the cation. The only "unusual" feature of the structures of 1 and 3 is the apparent formation of loosely bonded dimers due to stacking of overlapped imidazole rings where the two copper atoms are separated by distances of 3.198 Å and 3.466 Å respectively. Such metal–metal interactions are commonplace in the structures of cuprous complexes but Cu–Cu distances as long as these probably do not represent any significant bonding interaction [10]. Even for such a short Cu–Cu distance as 2.600 Å, as can be found in halogen-bridged halocuprates, the overlap population between the two copper atoms is small and negative (–0.015) [11]. For 6 there is likewise some evidence [1, 3] of a loose dimer formation, but this time with an apparent interaction between the copper atom and the C–C bond of a neighbouring pyrazole ligand with Cu–C distances of 3.150 and 3.221 Å. For 9 the structural data provide no indication of any specific bonding
interaction between the components of the crystal.

The determination of the complete $^{63}\text{Cu}$ coupling-constant tensor for both these and the pyridine complexes would certainly cast further light on this problem. We expect soon to be in a position to report the results for typical members of the pyridine series but, as mentioned above, we are uncertain as to the success of attempts to grow large single crystals of these very air-sensitive imidazole and pyrazole complexes.

4. Conclusion

The relationship between the $^{63}\text{Cu}$ NQR frequencies and the Cu–N bond lengths of the two-coordinated Cu(I) cations with imidazole or pyrazole ligands is markedly different from that of the analogous complexes with substituted pyridine ligands and this may imply a significant difference in electronic structure between these two series of complexes.

Acknowledgements

We thank the Swiss National Science Foundation for their support.

References