A ^{63,65}Cu and ^{127}I Nuclear Quadrupole Resonance and X-Ray Crystallographic Study of a Low-Temperature Phase of the *bis*(2-picoline) Copper(I) Iodide Dimer*

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Z. Naturforsch. **47a,** 106–110 (1992); received July 29, 1991

The temperature-dependence of the ^{63}Cu and ^{127}I NQR spectra of *bis*(2-picoline) Copper(I) Iodide reveals the existence of a phase change at 250 K. An X-ray crystallographic study of the low-temperature phase reveals that the iodine-bridged dimeric structure, which was observed at room-temperature, is retained in the low temperature phase but that the bond-lengths and, particularly, the bond-angles of the central four-membered ring are considerably modified.

Introduction

Our studies of the ^{63,65}Cu NQR spectra complexes of monovalent copper have, on a number of occasions, revealed the occurrence both of temperature-dependent phase-changes and of polymorphism. In contrast to the situation in organic compounds, where polymorphism is usually a question only of the packing together of essentially the same molecules, in these complexes the different phases often have notably different molecular geometries and are accompanied by significant changes in ^{63}Cu NQR frequencies [1, 2]. In order to further our understanding of the factors which determine the ^{63}Cu NQR frequency in these complexes we have undertaken a systematic study of such phase-changes. We have already reported results for dicoordinated cuprous cations [2], and report here the results of a study of a four-coordinated neutral complex.

Experimental

Preparations

The three *bis*(2-picoline) cuprous halide complexes were prepared according to the method described in [3, 4], namely recrystallisation of the cuprous halide from 2-picoline. All three complexes gave satisfactory elemental analyses.

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.

X-ray Crystallography

Single crystals were grown by slow controlled cooling (25 °C to -30 °C in 160 hours) of a solution of the complex in 2-picoline. A crystal was sealed in a Lindemann capillary under Argon to prevent degradation. Cell parameters and reflection intensities were measured at 190 K on a Nonius CAD4 diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å).

$C_{12}H_{14}N_2CuI$, mol. wt = 376.7, triclinic, space group $P'1$, $a = 8.0787(7)$, $b = 9.0632(8)$, $c = 10.3810(8)$ Å, $\alpha = 75.052(8)$, $\beta = 84.534(8)$, $\gamma = 67.853(7)°$, $V = 680.19(7)$ Å^3, $Z = 2$, $d_c = 1.84$ Mg · m^{-3}, $\mu = 3.83$ mm^{-1}, Fooo = 364. Data collection: $\sin\theta/\lambda < 0.58$,

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* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, United Kingdom, July 15–19, 1991.

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$h = -9.9$; $k = -10.10$, $l = 0.11$; $\omega/2\theta$ scans, no absorption correction. Of the 2188 measured reflections, 1905 considered as observed ($|Fo| > 4\sigma(Fo)$) and used in structure refinement. The structure was solved by direct methods (MULTAN-87) [5] and refined by least-squares analysis with XTAL-2.3 program [6]. Atomic scattering factors and anomalous-dispersion terms are taken from [7]. All coordinates of the H atoms were calculated. Final R factors: $R = 0.049$, $\omega R = 0.053$ ($\omega = 1/\sigma^2(Fo)$).

Calorimetry

Calorimetric measurements were carried out on a Setaram Model BT 2.15 microcalorimeter at a heating/cooling rate of 0.05 °C per minute. We thank Professor P. Tissot and Ms. H. Lartigue for carrying out these measurements.

Results

NQR

Most of the 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 relationship

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

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; this would be a difficult undertaking for the two phases of ((2-picoline)$_2$CuI)$_2$ which are the main subject of this report. However, even for an asymmetry parameter as great as 0.5, its effect on the resonance frequency is negligible compared to that of the coupling constant.

The temperature-dependence of the ^{63}Cu NQR frequency of the dimeric, iodine-bridged, complex ((2-picoline)$_2$CuI)$_2$ reveals a phase-transition at 256 K (Fig. 1), at which the ^{63}Cu resonance frequency increases by 0.8 MHz. The corresponding chloride and bromide, which have similar dimeric structures, show no evidence of this transition in the range 77 – 300 K, their frequencies varying smoothly in the usual manner with temperature. All these frequencies, together with their temperature dependence expressed as the coefficients of the relationship

$$\nu_T = \nu_0 + AT + BT^2 \tag{1}$$

are given in Table 1.

Table 1. Coefficients of the quadratic temperature-dependence (Eq. (1)) of the NQR frequencies of *bis*(2-picoline)copper(I) halides. For the ^{127}I resonances only the 1/2 – 3/2 transition could be observed.

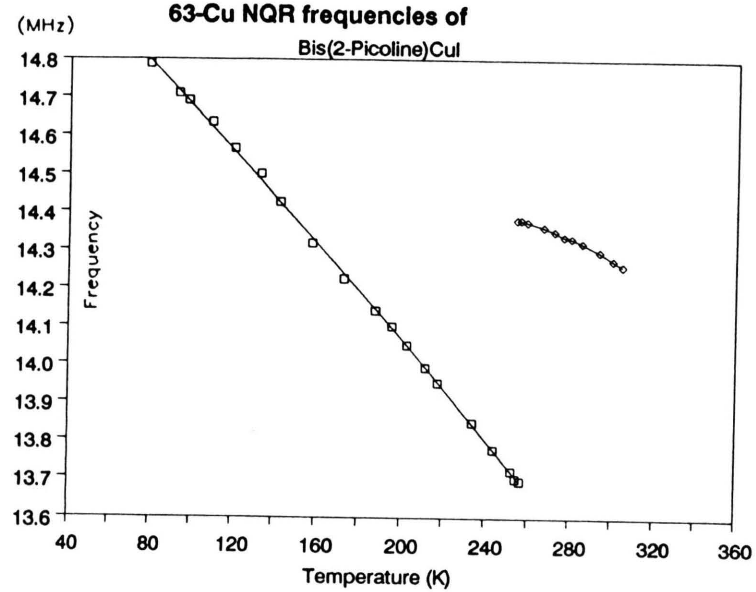
Complex	Nucleus	ν_0 (MHz)	A (kHz · deg^{-1})	B (Hz · deg^{-2})
[(2-picoline)$_2$CuCl]$_2$	^{63}Cu	15.855	−7.793	−3.184
[(2-picoline)$_2$CuBr]$_2$	^{63}Cu	17.568	−4.791	−8.555
	^{79}Br	41.915	−5.545	1.266
[(2-picoline)$_2$CuI]$_2$	^{63}Cu	15.229	−5.213	−3.088
	^{127}I	41.131	−12.254	75.913

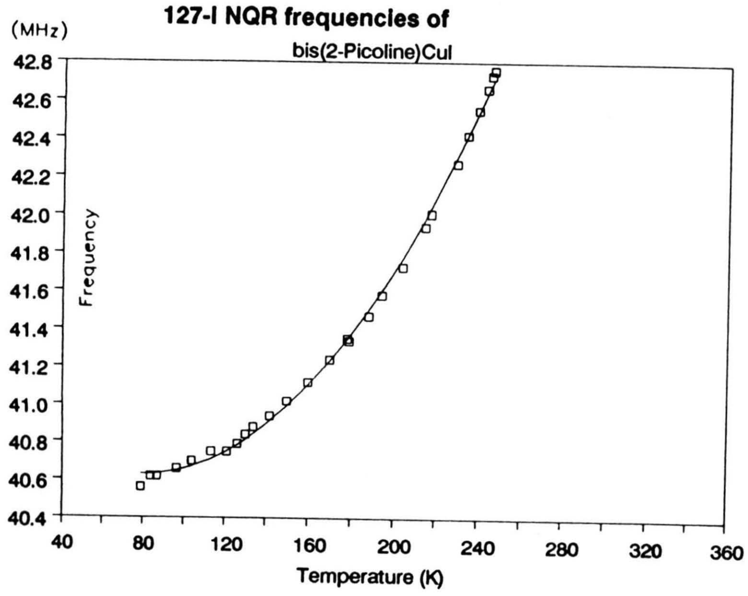
Table 2. Fractional coordinates and equivalent isotropic atomic displacement parameters with e.s.d.'s in parentheses for [(2-picoline)$_2$CuI]$_2$.

	x/a	y/b	z/c	U_{eq}^{*}
I	0.2449 (1)	0.06796 (9)	−0.09302 (8)	0.0279 (3)
Cu	−0.0824 (2)	0.1579 (2)	−0.1393 (2)	0.0309 (6)
N (101)	−0.077 (1)	0.387 (1)	−0.161 (1)	0.028 (4)
C (101)	0.081 (1)	0.406 (1)	−0.156 (1)	0.029 (5)
C (102)	0.096 (2)	0.554 (1)	−0.162 (1)	0.038 (6)
C (103)	−0.059 (2)	0.693 (1)	−0.172 (1)	0.034 (5)
C (104)	−0.221 (2)	−0.180 (1)	0.033 (5)	0.678 (1)
C (105)	−0.227 (1)	0.525 (1)	−0.176 (1)	0.028 (5)
C (106)	−0.401 (1)	0.504 (1)	−0.184 (1)	0.037 (5)
N (201)	−0.216 (1)	0.153 (1)	−0.2957 (9)	0.028 (4)
C (201)	−0.371 (2)	0.125 (1)	−0.273 (1)	0.034 (5)
C (202)	−0.479 (2)	0.138 (2)	−0.372 (1)	0.044 (6)
C (203)	−0.430 (2)	0.177 (2)	−0.502 (1)	0.060 (8)
C (204)	−0.271 (2)	0.204 (2)	−0.527 (1)	0.058 (8)
C (205)	−0.171 (2)	0.192 (2)	−0.422 (1)	0.040 (6)
C (206)	−0.002 (2)	0.229 (2)	−0.448 (1)	0.055 (7)

* U_{eq} is the average of the eigenvalues of U.

The phase transition is also evident from the ^{127}I spectrum, although in this case the resonances are detectable only in the low-temperature phase (Figure 2). The abnormal positive temperature coefficient is evidence of a rapidly-increasing amplitude of molecular motion as the transition temperature is approached. We were unfortunately unable to locate the 3/2 – 5/2 transition owing to a gap in our spectrometer coverage between 65 and 100 MHz; such an observation, by revealing the variation of all three components of the quadrupole coupling tensor, would have enabled a more complete discussion of this motion.





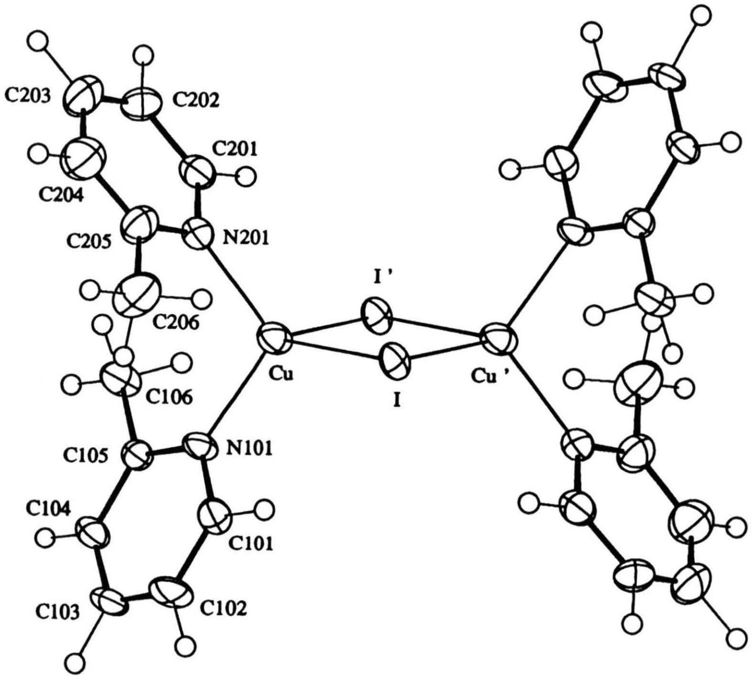


Fig. 3. Projection of the dimer [(2-picoline)$_2$CuI]$_2$ with 50% probability ellipsoids.

Fig. 1. The temperature dependence of the ^{63}Cu NQR frequency of [(2-picoline)$_2$CuI]$_2$.

Fig. 2. The temperature dependence of the ^{127}I NQR frequency of [(2-picoline)$_2$CuI]$_2$.

Table 3. Selected bond lengths (Å), bond angles (°) for [(2-picoline)$_2$CuI]$_2$. The primed atoms are obtained through the symmetry operation: $-x$, $-y$, $-z$.

	Low temp.[a]	High temp.[b]
I–I′	4.123 (1)	4.407 (3)
Cu–Cu′	3.452 (2)	3.083 (3)
Cu–I	2.719 (2)	2.714 (3)
Cu–I′	2.658 (1)	2.663 (3)
Cu–N (101)	2.05 (1)	2.05 (1)
Cu–N (201)	2.05 (1)	2.06 (1)
Cu–I–Cu′	79.89 (4)°	69.95 (6)°
I–Cu–I′	100.11 (5)°	110.05 (6)°
I–Cu–N (101)	110.3 (2)°	
I–Cu–N (201)	115.6 (2)°	
I′–Cu–N (101)	110.7 (3)°	
I′–Cu–N (201)	109.3 (3)°	
N (101)–Cu–N (201)	110.4 (4)°	117.9 (2)°
Angle between Cu$_2$I$_2$ plane and plane of ligand No. 1	65.8	73.5°
Angle between Cu$_2$I$_2$ plane and plane of ligand No. 2	51.4°	68.7°

[a] This work.

[b] Ref. [3].

X-ray Crystallography

Atomic coordinates and selected geometrical parameters are reported in Tables 2 and 3, respectively.

Calorimetric Measurements

On heating from 243 K to 273 K a first-order transition was observed at 257.8 K with an enthalpy change of 0.18 J g^{-1}, while on cooling over the same range the transition occurred at 254.6 K and an enthalpy change of 0.19 J g^{-1}.

Discussion

In the low temperature form the same dimeric structure is present but the central four-membered ring, formed by the two copper atoms and the two bridging iodine atoms, has been compressed along the I–I diagonal so that the CuICu angle increases from 70° to 80° and the Cu–Cu distance increases from 3.083 Å to 3.452 Å. Surprisingly, the increase in the ICuI angle is accompanied by an increase in the NCuN angle. The Cu–N distances are not measured with a very great precision in either of the two phases and there is no significant difference between them and, although the precision is higher in this case, the same is essentially true for the Cu–I distances.

While its shortcomings are manifest, the partial field-gradient model which has been developed, particularly in the field of Mössbauer spectroscopy, to account for the quadrupole coupling constants of polycoordinated nuclei [8], shows that, for tetrahedrally-coordinated nuclei such as these, the quadrupole coupling tensor is extremely susceptible to changes in the bond-angles. For tetrahedrally coordinated sites with C_{2v} symmetry, A_2B_2X, this model predicts the following relationship between the bond angles AXA (α) and BXB (β), the partial quadrupole coupling constants of the two ligands, e^2Qq^A and e^2Qq^B, and the principal values of the quadrupole coupling tensor of the central atom, X (The directions a, b, and c are, respectively, perpendicular to the AXA plane, perpendicular to the BXB plane and along the C_{2v} axis):

$$e^2Qq_{aa} = -e^2Qq^A + e^2Qq^B(3\sin^2\alpha - 1),$$
$$e^2Qq_{bb} = -e^2Qq^B + e^2Qq^A(3\sin^2\beta - 1),$$
$$e^2Qq_{cc} = e^2Qq^A(3\cos^2\alpha - 1) + e^2Qq^B(3\cos^2\beta - 1).$$

Approximate values of the partial ^{63}Cu coupling constants can be obtained from the resonance frequencies [3] of the neutral trigonal planar complexes formed between 2,6-lutidine and the cuprous halides, the monomeric L$_2$CuX complexes and the halogen-bridged dimers (LCuX)$_2$, where the direction of the z-component of the field-gradient tensor is certainly perpendicular to the molecular plane and its value thus independent of the bond-angles. The resonance frequency of these complexes is affected by the bond-angles only by their effect on the asymmetry parameter, and in this context the effect can safely be neglected. In this way we obtain 28.2 MHz for the partial ^{63}Cu coupling constant of the 2,6-lutidine ligand, and for the chloride, bromide and iodide ligands 21.0 MHz, 19.0 MHz and 17.0 MHz, respectively.

Table 4 shows the experimental resonance frequencies of these tricoordinated complexes, together with frequencies calculated from the above set of partial ^{63}Cu coupling constants. It has been assumed that there is no difference between the partial coupling constant produced by a terminal or a bridging halide. This assumption is probably justified within the limits of the partial field-gradient model. Finally, Table 5 shows the predicted components of the ^{63}Cu quadrupole coupling tensors and the resonance frequencies for the tetrahedral complexes, calculated from the above set of partial ^{63}Cu coupling constants and the

Table 4. Experimental and calculated ^{63}Cu NQR frequencies of tricoordinated planar complexes of 2,6-lutidine and the cuprous halides. The calculated resonance frequencies are obtained using the set of partial ^{63}Cu coupling constants given in the text.

Complex	^{63}Cu resonance frequency (MHz at 77 K)	
	Experimental	Calculated
(2,6-lutidine)$_2$CuCl	38.350	38.9
(2,6-lutidine)$_2$CuBr	37.614	37.9
(2,6-lutidine)$_2$CuI	36.132 [a]	37.1
(2,6-lutidine CuCl)$_2$	35.017 [b]	35.2
(2,6-lutidine CuBr)$_2$	33.0 [b,c]	33.2
(2,6-lutidine CuI)$_2$	31.37 [d]	31.6

[a] Average frequency for two different phases (36.964 and 35.300 MHz).

[b] A. Habiyakare and E. A. C. Lucken, unpublished measurements.

[c] Extrapolated from a frequency of 32.055 MHz at 305 K.

[d] Average of 31.656 and 31.085 MHz.

experimentally-determined molecular geometries. It can be seen that these "theoretical" resonance frequencies reproduce all the features of the experimental data: the difference between the high and the low temperature modifications of the iodide and the relative order of the resonance frequencies of the chloride, bromide and iodide. The partial coupling constant model also makes the prediction, as yet untested, that both the direction and the signs of the z-component of the ^{63}Cu tensor are different in the high and low temperature phases of the iodide.

Table 5. Calculated ^{63}Cu NQR frequencies of tetrahedrally coordinated complexes of 2-picoline and the cuprous halides. The calculated resonance frequencies are obtained using the set of partial ^{63}Cu coupling constants given in the text. The geometrical parameters for the chloride and bromide are taken from [4].

Complex	NCuN angle	XCuX angle	e^2Qq_{aa}	e^2Qq_{bb}	e^2Qq_{cc}	ν_q
[(2-picoline)$_2$CuCl]$_2$	122.1	100.3	−24.86	31.54	−6.68	16.24
[(2-picoline)$_2$CuBr]$_2$	124.0	99.6	−28.30	30.04	−9.74	19.76
[(2-picoline)$_2$CuI]$_2$ High temperature	117.9	110.0	−21.54	33.60	−12.06	17.02
[(2-picoline)$_2$CuI]$_2$ Low temperature	110.4	100.1	−30.34	23.74	7.60	15.78

Conclusion

The low-temperature phase of ((2-picoline)$_2$CuI)$_2$ has basically the same halogen-bridged dimeric structure as the high-temperature phase but the central four-membered ring has been compressed along the I–I diagonal. The decrease in ^{63}Cu NQR frequency which accompanies this phase-change can be explained on the basis of a partial coupling constant model together with the observed changes in molecular geometry.

Acknowledgements

We thank the Swiss National Research Fund for their support.

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