Crystallographic and Copper-63,65 Nuclear Quadrupole Resonance Study of Two-co-ordinated Copper(I) Cations with Hindered Substituted Pyridine Ligands*

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The crystal structures and ^{63,65}Cu NQR spectra are reported of the two-co-ordinated complex cations formed between Cu^I and hindered pyridine homologues, [CuL$_2$]X [L = 2,6-dimethylpyridine, X = BF$_4^-$ **1**, PF$_6^-$ **2** or ClO$_4^-$ (α phase) **3**, (β phase) **4**, (γ phase) **5**; L = 2,4,6-trimethylpyridine, X = BF$_4^-$ **6** or CuCl$_2^-$ **7**]. All complexes have essentially linear N–Cu–N fragments, but whereas for **1**, **2**, **4** and **6** the copper atom is located on a two-fold axis and the two pyridine rings have dihedral angles of 60.4, 56.0, 58.1 and 51.3° respectively, **3**, **5** and **7** have essentially planar structures with dihedral angles of 0, 3.0 and 0° respectively. In agreement with a previous study of the planar complex **3**, the Cu–N bond is significantly longer than in the non-planar conformation, and the corresponding ^{63,65}Cu NQR resonance frequencies are less.

It has recently been shown that the two-co-ordinated complex bis(2,6-dimethylpyridine)copper(I) perchlorate can adopt two distinct conformations.[1,2] Both forms have an essentially linear disposition of the two ligands and the central cation, but in one the lutidine ligands are coplanar while in the other,[2] although the structure was incorrectly described, the two lutidine fragments have a dihedral angle of about 60°. Presumably because of hindrance between the methyl groups of the two ligands, the Cu–N bond length in the coplanar form is somewhat longer than in the non-planar one.

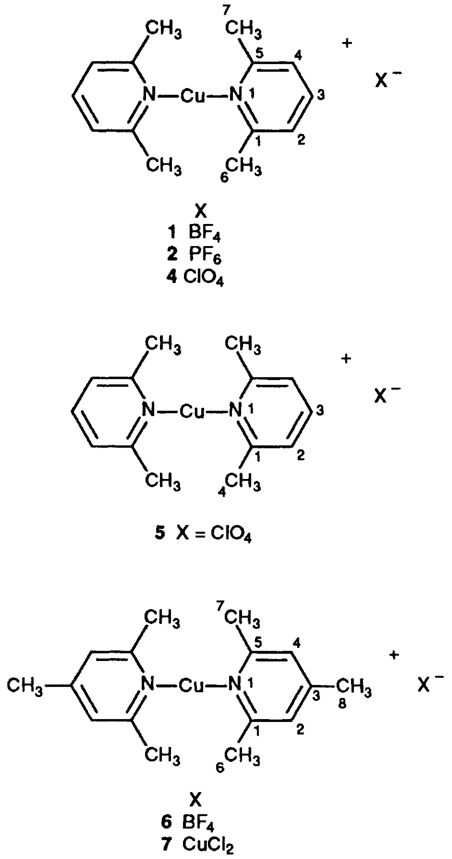
We have recently reported the ^{63,65}Cu NQR spectra of these two species[3] and observed that the NQR frequency of the planar variety with the longer Cu–N bond is some 1.7 MHz lower than that of the non-planar one. This is indeed the usual trend for a correlation between NQR frequency and bond length[4] and so we were led to postulate that the ^{63,65}Cu NQR frequencies would be diagnostic of the planar or non-planar geometry of such complexes. We report here the results of an NQR (compounds **1**–**7**) and X-ray crystallographic study (compounds **1**, **2** and **4**–**6**) which, while indicating clearly that the preferred geometry is non-planar, provided two further examples of a planar structure which strongly supports this hypothesis.

Experimental

Preparations.—The complexes [CuL$_2$]X were prepared according to the previously described method[3] and all gave satisfactory analyses for C, H and N while their IR spectra showed the presence of bands characteristic of the ligand and of the counter ion. Crystalline samples of the complexes were obtained in one of the following ways.

(*i*) For X$^-$ = BF$_4^-$, **1** and **6**, and CuCl$_2^-$ **7** the solution in ethanol was cooled slowly (1 week) from 40 to −20 °C in a computer-controlled cryostat.

(*ii*) For X$^-$ = PF$_6^-$ **2** a slow growth of crystals was obtained by allowing vapours of diethyl ether to diffuse slowly into a solution of the complex in acetone.



X
1 BF$_4$
2 PF$_6$
4 ClO$_4$

5 X = ClO$_4$

X
6 BF$_4$
7 CuCl$_2$

Scheme 1

(*iii*) The β polymorph of bis(2,6-dimethylpyridine)copper(I) perchlorate **4** was obtained as previously described[2,3] while the α and γ polymorphs **3** and **5** could be prepared from this by slow vapour diffusion of diethyl ether into a solution of the complex in a mixture of equal volumes of acetonitrile and 2,6-dimethyl-

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Summary of crystal data, intensity measurement and structure refinement for the two-co-ordinated copper(I) compounds*

Compound	**1**	**2**	**4**	**5**	**6**
Ligand	2,6-Dimethylpyridine	2,6-Dimethylpyridine	2,6-Dimethylpyridine (β)	2,6-Dimethylpyridine (γ)	2,4,6-Trimethylpyridine
Anion	BF_4	PF_6	ClO_4	ClO_4	BF_4
Formula	$C_{14}H_{18}BCuF_4N_2$	$C_{14}H_{18}CuF_6N_2P$	$C_{14}H_{18}ClCuN_2O_4$	$C_{14}H_{18}ClCuN_2O_4$	$C_{16}H_{22}BCuF_4N_2$
M	364.7	384.9	377.4	377.4	392.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Orthorhombic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*I*4$_1$/*acd*	*Pbcn*
a/Å	14.5880(12)	14.224(2)	14.504(2)	14.991(2)	16.1334(8)
b/Å	8.1910(7)	9.1042(14)	8.217(2)		7.7257(5)
c/Å	14.6791(10)	14.948(2)	14.878(5)	14.352(4)	14.6382(8)
β/°	113.12(1)	112.11(3)	112.54(1)	90	90
U/Å^3	1613.1(1)	1793.4(8)	1637.7(7)	3225(1)	1824.5(2)
Z	4	4	4	8	4
F(000)	744	856	776	1552	808
Crystal size/mm	0.17 × 0.25 × 0.37	0.15 × 0.32 × 0.35	0.09 × 0.20 × 0.20	0.15 × 0.17 × 0.22	0.13 × 0.22 × 0.32
D_c/mg mm^{-3}	1.50	1.57	1.53	1.55	1.43
μ(Mo-Kα)/mm^{-1}	1.39	1.36	1.53	1.55	1.24
$\sin(\theta/\lambda)_{max}$/Å^{-1}	0.60	0.60	0.60	0.66	0.60
No. measured reflections	1576	1763	2984	1166	1880
No. observed reflections	1168	1103	1783	416	1060
No. parameters	101	111	122	65	110
Max., average Δ/σ	0.036, 0.004	0.065, 0.014	0.000 04, 0.000 2	0.019, 0.002	0.055, 0.011
Max., min. Δρ (e Å^{-3})	+0.89, −0.74	+0.65, −0.88	+0.63, −0.98	+0.98, −0.91	+0.51, −0.62
S	3.35	4.22	2.67	2.18	2.93
R, R'	0.070, 0.059	0.074, 0.056	0.059, 0.046	0.048, 0.023	0.071, 0.056

* Details in common: criterion for observed reflections $|F_o| > 4\sigma(F_o)$; full-matrix refinement; weighting scheme $1/\sigma^2(F_o)$.

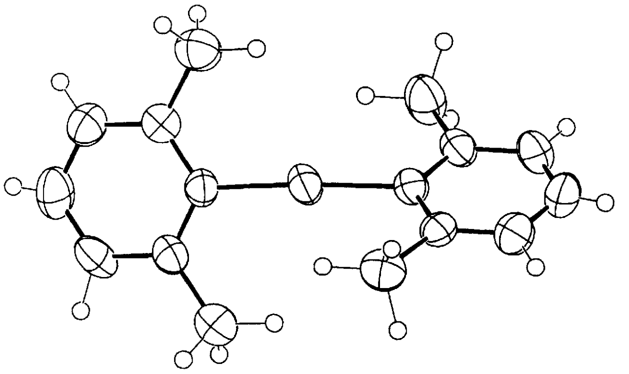

Fig. 1 Structure of the cation of complex **4** with atomic displacement parameters at 50% probability level. See Scheme 1 for atom labelling

pyridine. Which of the two polymorphs is actually obtained seems to be largely a matter of chance. When several containers filled with identical solutions of the complex in the acetonitrile–2,6-dimethylpyridine solvent were placed in the same enclosure and exposed to vapours of diethyl ether the resulting crystals within a given container were those of only one of the polymorphs, but different recipients contained different polymorphs. Since the vapour-diffusion method yielded large crystals of distinct habits there was no difficulty in distinguishing between the two polymorphs.

NQR Spectra.—The 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.—Cell parameters and reflection intensities were measured at room temperature on Nonius CAD-4 (for complexes **1** and **6**) and Philips PW1100 (for **2**, **4** and **5**) diffractometers with graphite-monochromated Mo-Kα radiation. A summary of crystal data, intensity measurements and structure refinements is given in Table 1. The atomic co-ordinates are reported in Table 2. Figs. 1 and 2 show the molecular structures of complexes **4** and **6**, while Figs. 3, 4 and 5 show projections of the unit cells of complexes **2**, **5** and **6**. The structures were solved by direct methods (MULTAN 87)[5] and refined by least-squares analysis with the XTAL program.[6] Atomic scattering factors and anomalous dispersion terms are taken from ref. 7. All co-ordinates of the hydrogen atoms have been calculated except for those of the three aromatic H atoms of **4** and all H atoms of **5** which we observed and refined with fixed isotropic displacement parameters. Selected geometrical parameters are reported in Table 3. Before becoming aware of the published structure of **7** we had independently solved this structure and obtained essentially the same results as those published.[8]

Additional material available in each case from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Structure of Compound **4**.—The structure of bis(2,6-dimethylpyridine)copper(I) perchlorate in its β phase was reported previously[2] as being monoclinic in the space group *Ia*. An analysis[9] of the coordinates shows that extra symmetry can be found in the structure. The complex has been resynthesised in our laboratory and a set of unique reflections and antireflections measured. A refinement in space group *C*2/*c* clearly confirms that this structure is centrosymmetric with the Cu and Cl atoms in special positions; all structural parameters of complex **4** are thus reported in space group *C*2/*c*. In particular, contrary to the results of Munakata *et al.*,[2] both Cu–N bond lengths are equivalent and the complex is isostructural with **1** and **2**.

Ordered and Disordered Anions.—In all complexes presented here the central atom of the anion is located on a special position. When the symmetry operation is a two-fold axis the sites of the atoms located out of the symmetry element are affected by large displacement parameters (complexes **2** and **6**)

Table 2 Atomic coordinates and population parameters (p.p.s) with estimated standard deviations (e.s.d.s) in parentheses for complexes **1**, **2** and **4**–**6**

	X/a	Y/b	Z/c	p.p. (if $\neq$ 1)
Compound **1**				
Cu	$\frac{1}{2}$	0.1171(2)	$\frac{1}{4}$	
N(1)	0.5885(3)	0.1080(7)	0.3858(3)	
C(1)	0.5622(4)	0.1747(8)	0.4569(5)	
C(2)	0.6259(5)	0.1625(9)	0.5562(4)	
C(3)	0.7141(5)	0.086(1)	0.5824(4)	
C(4)	0.7412(5)	0.0199(9)	0.5111(5)	
C(5)	0.6769(5)	0.0328(8)	0.4127(5)	
C(6)	0.4627(5)	0.2589(9)	0.4237(5)	
C(7)	0.7029(5)	−0.036(1)	0.3300(5)	
B	$\frac{1}{2}$	0.609(2)	$\frac{1}{4}$	
F(1)	0.5370(8)	0.671(2)	0.3432(8)	0.530(17)
F(2)	0.5968(7)	0.576(1)	0.2438(7)	0.462(8)
F(3)	0.561(1)	0.485(2)	0.2771(8)	0.395(10)
F(4)	0.515(1)	0.743(2)	0.313(1)	0.371(17)
F(5)	$\frac{1}{2}$	0.447(5)	$\frac{1}{4}$	0.176(17)
Compound **2**				
Cu	0.1217(2)	$\frac{1}{4}$	0.0517(9)	
N(1)	0.0848(4)	0.1168(8)	0.3830(4)	
C(1)	0.1783(6)	0.0511(9)	0.4109(6)	
C(2)	0.2389(6)	0.040(1)	0.5072(7)	
C(3)	0.2076(7)	0.097(1)	0.5759(6)	
C(4)	0.1142(7)	0.161(1)	0.5486(6)	
C(5)	0.0538(6)	0.1706(8)	0.4514(6)	
C(6)	0.2088(5)	−0.003(1)	0.3315(6)	
C(7)	−0.0495(6)	0.241(1)	0.4165(6)	
P	0	0.3831(6)	$\frac{3}{4}$	
F(1)	0	0.215(1)	$\frac{3}{4}$	
F(2)	0	0.549(1)	$\frac{3}{4}$	
F(3)	−0.0355(5)	0.388(1)	0.6416(4)	
F(4)	−0.1121(4)	0.3799(8)	0.7464(4)	
Compound **4**				
Cu	0	0.1296(2)	$\frac{1}{4}$	
Cl	0	0.6150(6)	$\frac{1}{4}$	
N(1)	0.0888(3)	0.1138(7)	0.3834(3)	
C(1)	0.0619(4)	0.1723(8)	0.4545(5)	
C(2)	0.1233(6)	0.157(1)	0.5505(5)	
C(3)	0.2123(6)	0.078(1)	0.5738(6)	
C(4)	0.2393(5)	0.021(1)	0.5028(6)	
C(5)	0.1771(5)	0.0386(9)	0.4062(5)	
C(6)	−0.0363(5)	0.259(1)	0.4249(5)	
C(7)	0.2045(5)	−0.019(1)	0.3251(5)	
O(1)	0.0293(6)	0.702(1)	0.3322(5)	
O(2)	0.097(1)	0.577(4)	0.240(2)	0.59(4)
O(3)	0.053(2)	0.473(3)	0.274(1)	0.46(4)
Compound **5**				
Cu	0	$\frac{1}{4}$	$\frac{1}{8}$	
N(1)	0.0915(2)	$-X + \frac{1}{4}$	$\frac{1}{8}$	
C(1)	0.0692(3)	0.0721(3)	0.1237(7)	
C(2)	0.1324(3)	0.0052(3)	0.1220(8)	
C(3)	0.2204(3)	$-X + \frac{1}{4}$	$\frac{1}{8}$	
C(4)	−0.0279(4)	0.0496(4)	0.121(1)	
Cl	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	
O	0.4564(3)	0.1859(3)	0.1825(2)	
Compound **6**				
Cu	0	0.4183(2)	$\frac{1}{4}$	
N(1)	0.0979(3)	0.4038(7)	0.1782(4)	
C(1)	0.1718(5)	0.457(1)	0.2104(5)	
C(2)	0.2447(4)	0.435(1)	0.1617(5)	
C(3)	0.2418(5)	0.358(1)	0.0762(5)	
C(4)	0.1652(5)	0.309(1)	0.0423(5)	
C(5)	0.0955(4)	0.3316(9)	0.0931(5)	
C(6)	0.1720(5)	0.543(1)	0.3028(5)	
C(7)	0.3202(5)	0.325(1)	0.0223(5)	
C(8)	0.0113(5)	0.275(1)	0.0601(5)	
B	$\frac{1}{2}$	0.406(3)	$\frac{1}{4}$	
F(1)	0.5143(6)	0.305(1)	0.3203(4)	
F(2)	0.5656(4)	0.5045(9)	0.2398(7)	

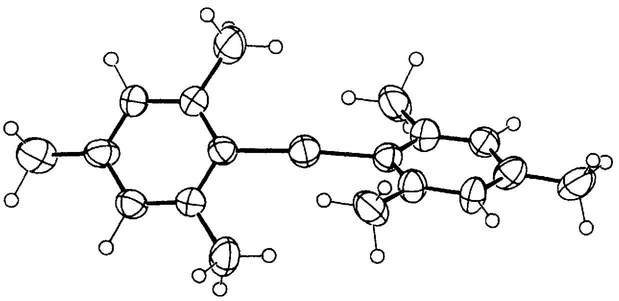

Fig. 2 Structure of the cation of complex **6** with atomic displacement parameters at 50% probability level

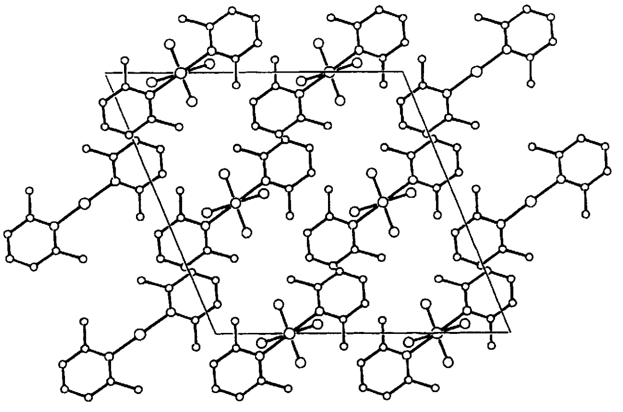

Fig. 3 Unit-cell contents of complex **2** projected along the *b* axis. Complexes **1** and **4** are isostructural

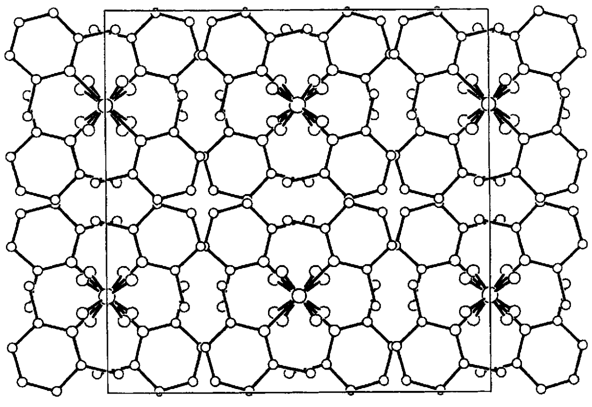

Fig. 4 Unit-cell contents of complex **5** projected along the *c* axis

or exhibit disorder (complexes **1** and **4**). The BF_4^- anion of **1** is disordered and five atomic sites have been observed and refined for the F atoms. The refinement of their population parameters led to values between 0.18 and 0.53 with a sum of 1.93 compared with an expected value of 2.0. The ClO_4^- anion of **4** is also disordered and three independent sites for the oxygen atoms have been refined of which only two are partially occupied [population parameters: O(1) 1.00(2), O(2) 0.59(4), O(3) 0.46(4)].

Nuclear Quadrupole Resonance Frequencies.—The $^{63,65}Cu$ NQR resonance frequencies of these complexes, measured at 77 K, are shown in Table 4. The temperature dependence of these frequencies, F_T, was observed in the range 77–300 K and the results fitted to a quadratic (1). The parameters of equation

$$F_T = F_0 + AT + BT^2 \qquad (1)$$

(1) for all the complexes are also given in Table 4. The temperature dependences all follow the usual pattern with both

Table 3 Selected geometrical parameters (distances in Å, angles in °) of two-co-ordinated copper complexes

Compound	1	2	3[a]	4	5	6	7[b]
Ligand	2,6-Dimethylpyridine	2,6-Dimethylpyridine	2,6-Dimethylpyridine (α)	2,6-Dimethylpyridine (β)	2,6-Dimethylpyridine (γ)	2,4,6-Trimethylpyridine	2,4,6-Trimethylpyridine
Anion	BF_4	PF_6	ClO_4	ClO_4	ClO_4	BF_4	$CuCl_2$
Symmetry at Cu	Two-fold axis	Two-fold axis	Inversion centre	Two-fold axis	Three two-fold axes	Two-fold axis	Inversion centre
Cu-N	1.904(4)	1.898(5)	1.936(5)	1.912(4)	1.939(3)	1.900(5)	1.923(3)
N-Cu-N	175.6(3)	177.3(2)	180	172.2(3)	180	173.2(3)	180
$CH_3 \cdots CH_3$	4.297(9)	4.181(11)	3.67(1)	4.251(10)	3.658(8)	4.131(11)	3.65(1)
Min. Cu ··· anion	2.70(4)	2.999(11)	2.984(6)	2.91(2)	2.997(4)	3.169(8)	3.344(2)
Dihedral angle between the two substituted pyridines	60.4(2)	56.0(2)	0	58.1(3)	3.0(3)	51.3(2)	0

[a] Ref. 1. [b] Ref. 8.

Table 4 Copper-63 NQR frequencies measured at 77 K and their temperature dependence, fitted to the equation $F_T = F_0 + AT + BT^2$; ^{65}Cu resonance frequencies having values 0.925 times those of the corresponding ^{63}Cu resonances were observed in all cases

Complex	F_{77}/MHz	F_0/MHz	A/kHz K^{-1}	B/Hz K^{-2}
1	41.275	41.485	−2.274	−4.012
2	41.951	42.149	−1.798	−7.189
3	39.400	39.639	−2.212	−6.378
4	40.892	41.133	−2.455	−3.312
5	39.203	39.492	−3.133	−4.688
6	41.170	41.469	−2.853	−4.685
7	39.775	39.985	−2.871	−5.300
7 (anion)	30.428	30.641	−2.000	−5.200

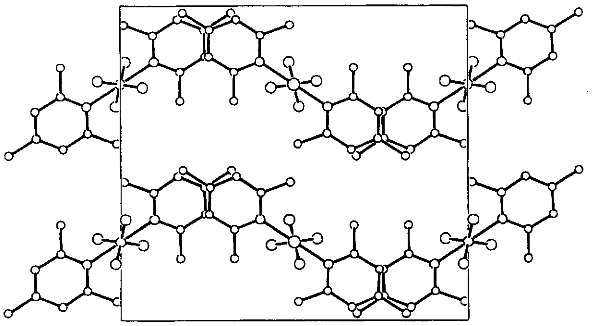

Fig. 5 Unit-cell contents of complex 6 projected along the *b* axis

parameters *A* and *B* being negative and with the frequency at 300 K being around 1.0 MHz less than that at 77 K. For bis(2,4,6-trimethylpyridine)copper(I) dichlorocuprate(I) 7 the ^{63,65}Cu resonances of the anion were also observed and are likewise reported in Table 4.

Discussion

Isomorphism and Polymorphism of Bis(2,6-*dimethylpyridine*)-*copper*(I) *Complexes*.—The BF_4 (**1**), PF_6 (**2**) and ClO_6 (β phase) (**4**) complexes are isomorphous and characterized by a two-fold symmetry of the cation with a dihedral angle between the pyridine rings of 60.4, 56.0 and 58.1° respectively. The copper(I) and the central atom of the anion are located in special positions (4e) on a two-fold axis.

The ClO_4 complex exists in three polymorphous phases, each exhibiting a distinct symmetry of the cation: an inversion centre for the α phase **3**[1] with the Cu atom in position 4a, a two-fold axis in the β phase **4** with the Cu atom in position 4e and three two-fold axes in the γ phase **5** with the Cu atom in position 8b. The last phase is isostructural with that of the analogous silver(I) complex.[1]

Site Symmetry at the Copper(I) *Atom in* 2,4,6-*Trimethylpyridine Complexes*.—The Cu atom of the BF_4 complex **6** is located on a two-fold axis (position 4c) with a dihedral angle of 51.3(3)° between the pyridine rings whereas in the $CuCl_2$ complex **7** it is on an inversion centre (position 2d) with two coplanar pyridine rings.[8]

In all structures, the anions (A) and the copper atoms of the complexes are alternately distributed along a crystallographic axis in a sequence ··· Cu ··· A ··· Cu ··· A ···. In **7** this sequence is respected with an alternation of the copper atoms of the complex and the copper atom of the dichlorocuprate anion [Cu ··· Cu 3.611(2) Å[8]]. It should be noted that in **2** two fluorine atoms are located on the same two-fold axis as the Cu and P atoms, leading to the formation of linear chains ··· Cu ··· F–P–F ··· Cu ··· F–P–F ··· parallel to the *b* axis. The anion can be considered as co-ordinated (see Table 3).

The ligand geometries are consistent with those of previously reported analogous compounds and the angular asymmetry at the C(2)-methyl substituent confirms the general trend to be bent toward the copper atom in spite of steric interactions with the opposite methyl ligand [mean angles N–C–CH_3 117.1(7) and CH_3–C–C 121.5(1.3)°]. The coherence of the Cu–N bond lengths between the planar [mean 1.933(8) Å] and non-planar complexes [mean 1.904(6) Å] can be considered as excellent.

Nuclear Quadrupole Resonance Frequencies.—For a spin $\frac{3}{2}$ nucleus such as ^{63}Cu the resonance frequency is given by the expression (2) where e^2Qq is the nuclear quadrupole coupling

$$F = e^2Qq/2(1 + \eta^2/3)^{\frac{1}{2}} \qquad (2)$$

constant and η is the asymmetry parameter. These two parameters can only be extracted from the resonance frequency by Zeeman-perturbed NQR studies of large (1 cm^3) single crystals which we have, so far, been unable to prepare.

In accordance with our previous hypothesis, the resonance frequencies of the three planar complexes are noticeably less than those of the four non-planar ones. Fig. 6 shows the correlation between the Cu–N bond length, *l* (in Å), and the ^{63}Cu resonance frequency (F_{77}), measured at 77 K, of the compounds discussed here, together with those previously reported. The linear regression is given by equation (3) with a correlation coefficient $R = 0.98$.

$$F_{77} = 157.661 - 61.136l \text{ MHz} \qquad (3)$$

An alternative or additional source of the difference between the planar and the non-planar complexes arises if there is significant π bonding (d_π–p_π or p_π–p_π) between the copper atom and the π orbitals of the ligands. If this occurs one would anticipate a considerable difference between the planar and the

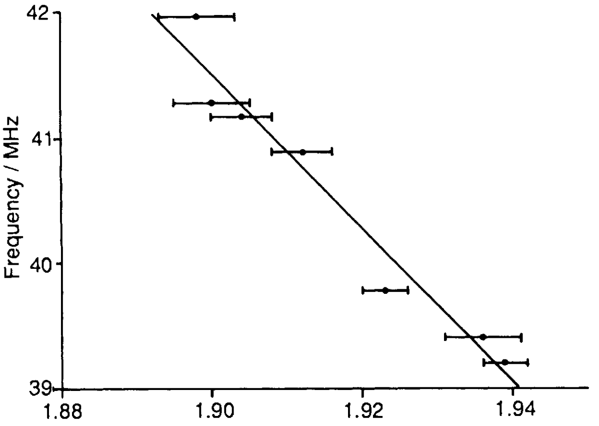

Fig. 6 Correlation between Cu–N bond length and ^{63}Cu NQR frequency

non-planar complexes which could, depending on the balance between the σ- and π-interactions, yield a decrease in the coupling constant of the planar complexes. Such an interaction would, however, also produce a marked increase in the asymmetry parameter of the planar complexes and we hope to investigate this point when we have succeeded in preparing large single crystals of these complexes.

Acknowledgements

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