Nuclear Quadrupole Resonance and Crystallographic Studies of Three-co-ordinated Copper(I) Cations with Alkylpyridine Ligands*

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The preparation and ^{63,65}Cu NQR resonance frequencies of fourteen three-co-ordinated complex cations of copper(I) with alkylpyridine ligands are reported. Crystal structures of seven of these have also been determined. The complexes show a wide variety of symmetries but in none does the copper atom lie on an ideal three-fold axis. In most the copper lies in an essentially trigonal-planar environment but with at least two of the pyridine ligands twisted well out of the plane containing the copper and the three nitrogen atoms. In most cases one of the N–Cu–N bond angles is significantly greater than 120° while the length of the opposing bond is significantly greater than that of the two bonds that form this angle. All the NQR frequencies at 77 K are in the neighbourhood of 45 MHz, with the exception of that of the complex with 3,5-dimethylpyridine, the only ligand without at least one alkyl substituent *ortho* to the nitrogen atom, where the frequency at 77 K is 40.471 MHz. This difference results from the axial co-ordination of both the PF_6 anions to the copper cation.

In the course of an investigation of the ^{63,65}Cu NQR resonance frequencies and crystal structures of two-co-ordinated copper(I) cations with hindered pyridine ligands[1,2] we discovered methods for the preparation of the analogous three-co-ordinated cations. The crystal structure of tris(2-methylpyridine)copper(I) perchlorate was reported in 1972,[3] but although three-co-ordinated copper(I) complexes are not uncommon they are usually neutral species, and we are not aware of any reports of the preparation or structures of any other such complex cations with substituted pyridine ligands. We therefore report here the preparation and the ^{63,65}Cu NQR resonance frequencies of fourteen three-co-ordinated complexes, $[CuL_3]X$, with alkylpyridine ligands, and the crystal structures of seven of the complexes, **1**, **4**, **5**, **7**, **10**, **13**, and **14**.

Experimental

Preparations.—The following general method applies to all the hexafluorophosphates. A solution of copper(II) sulfate pentahydrate (0.02 mol) in water (100 cm^3) was reduced with ascorbic acid (0.01 mol) in the presence of an excess (0.1 mol) of ligand. The mixture was vigorously stirred at room temperature and became a pale yellow. To this solution was added a slight excess (0.025 mol) of potassium hexafluorophosphate in water (50 cm^3). The resultant precipitate was filtered off, washed and dried. With heavily hindered ligands such as 2,6-dimethylpyridine the three-co-ordinated complex may be obtained by crystallisation of this precipitate either from the pure ligand or from acetone containing an excess of the ligand (0.1 mol), whereas crystallisation from ethanol yields the two-co-ordinated complex. With less-hindered ligands the three-co-ordinated complex is also obtained by recrystallisation from ethanol containing an excess of the ligand. For the perchlorates, **2**, **6**, **8** and **12**, and for the tetrafluoroborate, **9**, copper(II) perchlorate or tetrafluoroborate was mixed with the same proportions of ligand and ascorbic acid in either acetone (for heavily hindered ligands) or ethanol. The solution was brought to boiling and filtered hot; the complex crystallised from the cooled filtrate. Crystals suitable for structure determination were prepared by slow diffusion of diethyl ether vapour into a solution of the complex in acetone. When excessive drying, leading to loss of ligand, was avoided all complexes gave satisfactory carbon, hydrogen and nitrogen analyses (Table 1) (Dr. H. Eder, University of Geneva Microanalytical Laboratory).

NQR Spectroscopy.—The NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. The uncertainty in the frequency measurements depends on the linewidths of the various resonances, typically of the order of 2–3 kHz, as well as on the precision of the temperature measurement since the resonance frequencies have temperature coefficients of the order of -10 kHz K^{-1}. The resulting uncertainty in the resonance frequencies is thus typically ± 5 kHz. 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.—Crystals were sealed in Lindemann capillaries under argon to prevent degradation. Cell parameters and reflections intensities were measured at room temperature on Nonius CAD-4 (**1**, **5** and **14**) and Philips PW1100 (**4**, **7**, **10** and **13**) diffractometers with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å). Data were corrected for Lorentz and polarisation effects but not for absorption ($\mu r < 0.25$). A summary of crystal data, intensity measurements and structure refinements is given in Tables 2 and 3. The atomic coordinates are reported in Table 4. The structures were solved by direct methods (MULTAN 87)[4] and refined by least squares with the XTAL 3.0 program.[5] Atomic scattering factors and anomalous

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Microanalytical data for the $[CuL_3]X$ complexes

Complex	L	X	Analysis (%)* C	H	N
1	2-methylpyridine	PF_6	44.15 (44.30)	4.15 (4.35)	8.50 (8.05)
2	2-ethylpyridine	ClO_4	48.05 (52.05)	5.60 (5.60)	8.05 (8.65)
3	2-benzylpyridine	PF_6	60.55 (60.35)	4.65 (4.65)	5.90 (5.85)
4	2,3-dimethylpyridine	PF_6	47.50 (47.60)	5.05 (5.15)	7.80 (7.90)
5	2,5-dimethylpyridine	PF_6	47.50 (47.60)	5.10 (5.15)	7.90 (7.90)
6	2,5-dimethylpyridine	ClO_4	51.75 (52.05)	5.40 (5.60)	8.50 (8.65)
7	2,6-dimethylpyridine	PF_6	47.05 (47.60)	5.10 (5.15)	7.85 (7.90)
8	2,6-dimethylpyridine	ClO_4	50.95 (52.05)	5.30 (5.60)	8.60 (8.65)
9	2,6-dimethylpyridine	BF_4	51.05 (53.45)	5.40 (5.75)	8.55 (8.90)
10	3,5-dimethylpyridine	PF_6	47.45 (47.60)	5.20 (5.15)	7.80 (7.90)
11	5-ethyl-2-methylpyridine	PF_6	50.25 (50.40)	5.75 (5.80)	7.25 (7.35)
12	5-ethyl-2-methylpyridine	ClO_4	53.85 (54.75)	6.25 (6.30)	7.75 (8.00)
13	5-butyl-2-methylpyridine	PF_6	54.60 (54.90)	6.80 (6.90)	6.30 (6.40)
14	2,4,6-trimethylpyridine	PF_6	50.25 (50.40)	5.65 (5.80)	7.20 (7.35)

* Required values are given in parentheses.

dispersion terms were taken from ref. 6. All coordinates of the hydrogen atoms have been calculated. Selected geometrical parameters are reported in Table 5. In all cases of ambiguous space group attribution the data collection was made in the corresponding non-centrosymmetric space group with measurement of a set of unique reflections and antireflections.

All crystal structures show disorder or large values of atomic displacement parameters (anionic and/or cationic fragments) which explains the relatively large *R* values reported in Tables 2 and 3. Thus the diffracted intensities decreased rapidly and led to a lack of information at high θ. This situation, common to all disordered or partially disordered crystal structures, directly affects the estimation of atomic displacement parameters in the refinement, and can lead, with the use of a statistical weighting scheme [*i.e.*, $1/\sigma^2(F_o)$] to a non-physical representation of some displacement parameters (negative determinant of the tensor). For this reason, compounds **4**, **10** and **13** were refined with unit weights, which is detrimental to the *R* values. In all other cases a weighting scheme $1/\sigma^2(F_o)$ was applied and the weighted function refined. Nevertheless the unit-weighting scheme used in the analysis did not produce less-precise results than schemes based on counting statistics.[7]

It should be noted that compounds **5** and **10** belong to the same space group and have similar values of the unit-cell parameters *a* and *c* while the value of *b* for **5** is about twice that for **10**. Although the cationic part of the molecules is oriented in the same direction (co-ordination plane parallel to the *ac* plane), the molecular symmetries differ and the compounds could not be considered as isostructural (see Figs. 1, 5 and 6).

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

Results

Structures.—The PF_6 anions of complexes **1** and **14** show no disorder, whereas for all other complexes the fluorine atoms are disordered. For each disordered case the sites of the F atoms have been refined with isotropic atomic displacement parameters and appropriate occupancy factors. All structures affected by this disorder show large values of Δ/σ in the final refinement due to the variation of the atomic displacement parameters of the disordered F atoms, and relatively large final $\Delta\rho$ (e $Å^{-3}$), always located in the proximity of the P atom of the disordered anion.

The absolute configuration of complex **7** has been established by refinement of the enantiomorph polarity parameter[8] [$x = -0.01(6)$] and corresponds to the set of coordinates given in Table 4. The structure of **13** shows a disordered orientation of the butyl chain attached to the pyridine located on the mirror plane. This disorder has been solved by splitting the coordinates of five atomic sites and refining them with population parameters of 0.5. It should be noted that the refinement of this structure in the space group $Pna2_1$ (loss of the mirror plane and inversion centre) shows the same disorder and leads to a value of the enantiomorph polarity parameter *x* of 0.5. This could indicate that the crystal was twinned by inversion or centrosymmetric.

NQR Spectroscopy.—The ^{63}Cu resonance frequencies, measured at 77 K, are reported in Table 6. The temperature dependence of the frequencies was determined in the range of 77 K to room temperature and the results fitted to the quadratic equation (1). The coefficients are shown in the table.

$$\nu_T = \nu_0 + AT + BT^2 \qquad (1)$$

The temperature dependence of the NQR spectra of three of the complexes **5**, **7** and **10** shows a discontinuity indicative of a phase change between 77 K and room temperature. This behaviour is shown in Figs. 7–9. Thus, below 85 K, **5** changes to a phase where there are two inequivalent complexes in the unit cell while for **7** there are three inequivalent molecules below 155 K. Complex **10**, on the other hand, still has only one inequivalent molecule in the unit cell but the sharp discontinuity and the totally different temperature dependence of the resonance frequency in the low-temperature region is clear evidence of a phase change. Complex **12** only shows a resonance above 234 K; this too may either indicate that a phase change has taken place at this temperature or that some slow reorientation process, that broadens the line, occurs at low temperatures.

Of those complexes whose structures we have not determined, the multiplicity of the NQR resonances shows that **2**, **3**, **11** and **12** have only one distinct molecule in the unit cell while the unit cells of **6** and **8** contain two and of **9** three inequivalent molecules. We were unable to observe any resonances from tris(2-methylpyridine)copper(I) perchlorate, whose structure has previously been reported.[3]

Discussion

Structures.—The three-co-ordinated copper(I) complexes adopt a wide variety of symmetries [two-fold axis (**7**, **14**), mirror plane (**5**, **13**) or both for the same molecule (**10**)] but never an ideal three-fold axis. Nevertheless, at least four of them [**5**, **7**, **10** and **14** (molecule 2)] exhibit an intramolecular symmetry close to C_3, the closest approach being observed for molecule 2 of complex **14**.

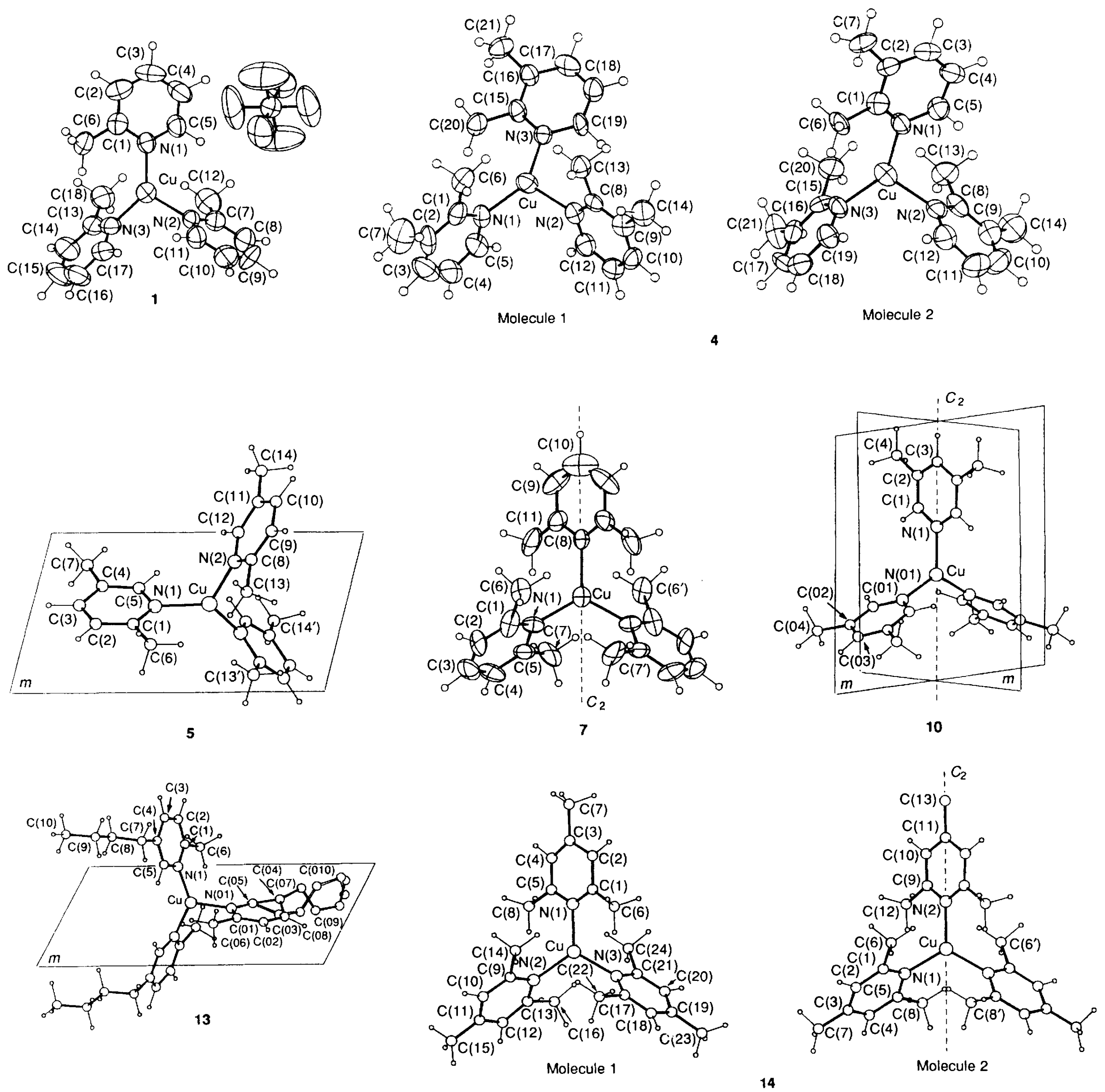

Fig. 1 Molecular structures of three-co-ordinated copper(I) complexes showing atomic numbering and symmetries. Ellipsoids are represented with 50% probability for **1** and **4**, and with 40% probability for **10**. For the other compounds arbitrarily fixed atomic radii are used in order to clarify the diagrams

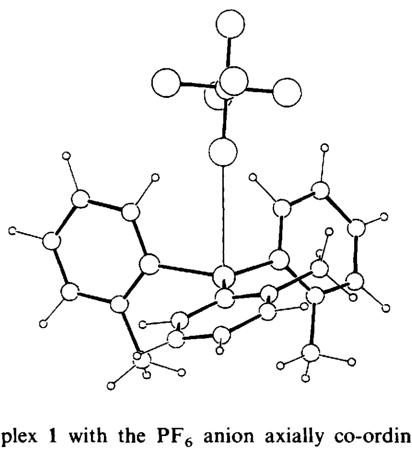

Fig. 2 Complex **1** with the PF_6 anion axially co-ordinated to the copper atom

For all complexes, including tris(2-methylpyridine)copper(I) perchlorate,[3] the co-ordination sphere of the copper atom is essentially planar [maximum distance of Cu from plane of the three co-ordinated N atoms is 0.206(8) Å] and almost trigonal (see Table 5). The opening of the N–Cu–N angle is correlated with the orientation of co-ordinated pyridines and shows a wide variation (106.1–141.4°). Thus, the higher N–Cu–N angles 135.3, 141.5 and 141.3° are observed for **1** and **4** where the dihedral angles (φ) between the co-ordination plane and the mean planes of one of the pyridines are 18.8, 4.1 and 26.4° respectively. Complex **13** exhibits a large value of the N–Cu–N angle (137.7°) although the dihedral angles are close to 90°; this may be due to the presence of the bulky substituent in the 5 position. The observation of a pyridine plane that is almost coplanar to the co-ordination plane seems to result essentially from two kinds of intermolecular interactions. The crystals being ionic, the copper atom could have an extra axial co-ordination with the anion, requiring the cation to adapt the

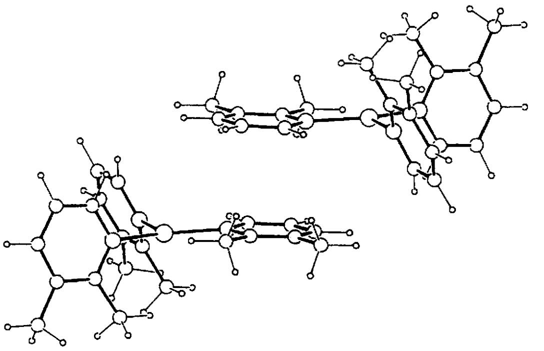

Fig. 3 Molecule 1 of complex **4** showing the stacking interaction of the two pyridines almost parallel to the co-ordination plane through the inversion centre at $\frac{1}{2}$,0,$\frac{1}{2}$

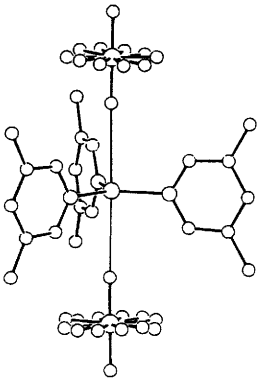

Fig. 4 Complex **10** with the two axially co-ordinated PF_6 anions. The Cu $\cdots$ F bonds are parallel to the *b* axis and the four disordered fluorine atoms (12 sites) are approximately located on the *ac* plane

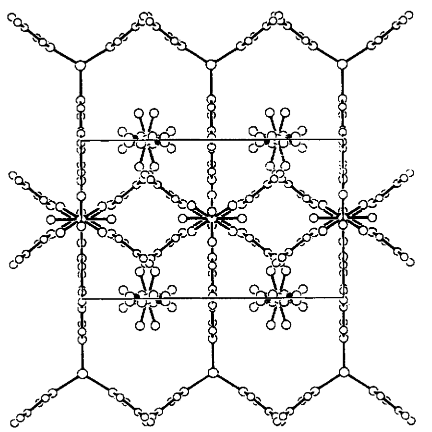

Fig. 5 Unit-cell contents of complex **5** projected along the *b* axis showing the pseudo-C_3 symmetry of the cation

dihedral angles of the co-ordinated pyridines to satisfy this extra co-ordination. This is clearly the case in complex **1** where the PF_6 anion is weakly co-ordinated to the copper atom [Cu $\cdots$ F 3.356(6) Å]. This co-ordination is almost perpendicular to the N_3 plane. Of the ligating pyridines monosubstituted at position 2, two have the methyl group on one side of the co-ordination plane and the third one is aligned parallel to the CuN_3 plane allowing the anion to be co-ordinated on the opposite, less-hindered face (Fig. 2). Another case of intermolecular interactions leading a pyridine to adopt an orientation almost parallel to the co-ordination plane is observed in **2**. In this complex each independent molecule of the asymmetric unit is involved in stacking interactions with its centrosymmetric equivalent through the inversion centres at $\frac{1}{2}$,0,$\frac{1}{2}$ and $\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$ for molecules 1 and 2 respectively. The mean distances between the two stacked pyridines are 3.66 and 3.68 Å for molecules 1 and 2. The two pyridines not involved in the stacking interaction are oriented so that their substituents point to the opposite side of the stacking plane (Fig. 3). Consequently, in both cases mentioned above, the pyridine that is almost parallel to the co-ordination plane has its methyl group pointing toward the adjacent ligand and the N–Cu–N angle increases significantly.

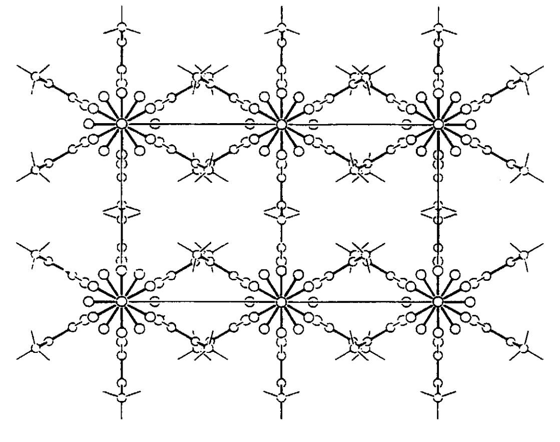

Fig. 6 Unit-cell contents of complex **10** projected along the *b* axis showing the pseudo-C_3 symmetry of the cation

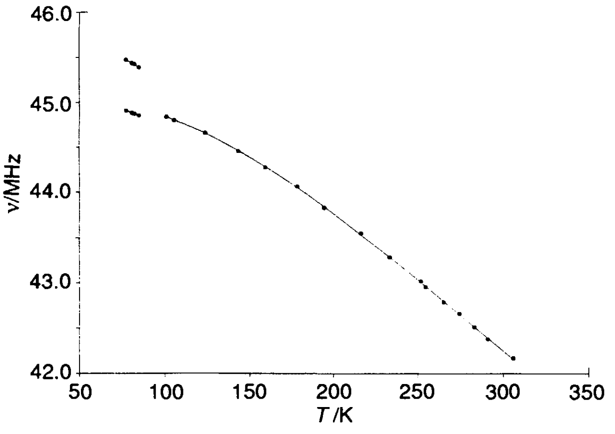

Fig. 7 The temperature dependence of the ^{63}Cu NQR frequencies of complex **5**

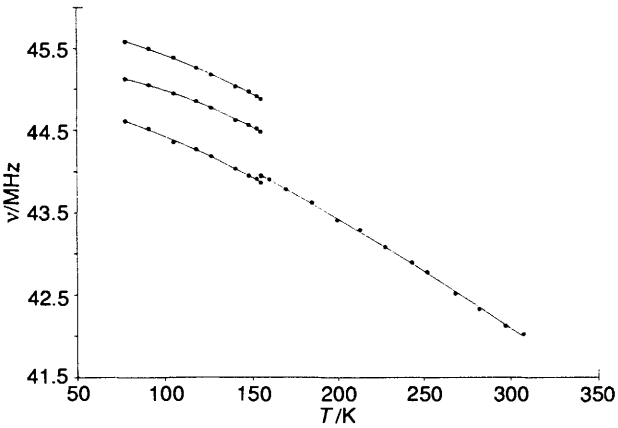

Fig. 8 The temperature dependence of the ^{63}Cu NQR frequencies of complex **7**

As would be expected from considerations concerning orbital overlap, confirmed by extended-Hückel and *ab initio* calculations,[9] the length of the Cu–L bond opposite to the largest

Table 2 Summary of crystal data, intensity measurement and structure refinement for the three-co-ordinated copper(I) dimethylpyridine complexes *

Compound	**4**	**5**	**7**	**10**
Ligand	2,3-Dimethylpyridine	2,5-Dimethylpyridine	2,6-Dimethylpyridine	3,5-Dimethylpyridine
Diffractometer	Philips PW1100	Nonius CAD4	Philips PW1100	Philips PW1100
Crystal system	Triclinic	Orthorhombic	Trigonal	Orthorhombic
Space group	$P\bar{1}$	*Cmma*	$P3_121$	*Cmma*
a/Å	10.589(3)	14.660(2)	11.770(1)	15.502(3)
b/Å	15.354(3)	37.595(3)	—	18.373(2)
c/Å	15.721(3)	8.959(1)	16.290(3)	8.364(2)
α/°	107.10(1)	90	90	90
β/°	95.11(1)	90	90	90
γ/°	94.86(1)	90	120	90
U/Å^3	2416.7(9)	4938(1)	1954.4(4)	2524.6(9)
Z	4	8	3	4
F(000)	1088	2176	816	1088
Crystal size/mm	0.10 × 0.20 × 0.20	0.18 × 0.20 × 0.24	0.20 × 0.20 × 0.20	0.18 × 0.25 × 0.26
D_c/mg mm^{-3}	1.457	1.426	1.351	1.394
μ(Mo-Kα)/mm^{-1}	1.027	1.006	0.953	0.983
$[(\sin\theta/\lambda]_{max}$/Å^{-1}	0.51	0.53	0.51	0.62
No. measured reflections	5192	3260	3196	2670
No. unique reflections	5192	1630	1409	1335
No. observed reflections	3010	969	935	834
No. parameters	557	162	145	109
Weighting scheme	1	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	1
Maximum and average Δ/σ	0.516, 0.016	0.126, 0.023	0.055, 0.010	0.422, 0.039
Maximum and minimum $\Delta\rho$/e Å^{-3}	+1.0, −1.2	+0.72, −0.73	+0.60, −0.82	+0.43, −0.56
Enantiomorph polarity x	—	—	−0.01(6)	—
S	3.99	2.46	3.24	2.78
R, R'	0.090, 0.090	0.078, 0.051	0.079, 0.044	0.056, 0.056

* Details in common: formula $[Cu(C_7H_9N)_3]PF_6$; molecular weight 530.0; criterion for observed reflections $|F_o| > 4\sigma(F_o)$; full-matrix refinement.

Table 3 Summary of crystal data, intensity measurement and structure refinement for the three-co-ordinated copper(I) complexes **1**, **13** and **14** *

Compound	**1**	**13**	**14**
Ligand	2-Methylpyridine	5-Butyl-2-methylpyridine	2,4,6-Trimethylpyridine
Formula	$[Cu(C_6H_7N)_3]PF_6$	$[Cu(C_{10}H_{15}N)_3]PF_6$	$[Cu(C_8H_{11}N)_3]PF_6$
M	487.9	656.2	572.1
Diffractometer	Nonius CAD4	Philips PW1100	Nonius CAD4
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*Pnma*	*C*2
a/Å	9.745(2)	21.648(5)	20.601(3)
b/Å	14.243(2)	16.513(2)	12.024(1)
c/Å	16.053(4)	9.487(1)	17.640(2)
β/°	106.67(1)	90	98.153(8)
U/Å^3	2134.5(8)	3391.4(9)	4325.5(9)
Z	4	4	6
F(000)	992	1376	1776
Crystal size/mm	0.17 × 0.17 × 0.22	0.15 × 0.22 × 0.25	0.15 × 0.25 × 0.27
D_c/mg mm^{-3}	1.518	1.290	1.318
μ(Mo-Kα)/mm^{-1}	1.156	0.745	0.866
$[(\sin\theta)/\lambda]_{max}$/Å^{-1}	0.55	0.51	0.55
No. measured reflections	3074	3786	3145
No. unique reflections	2832	1893	2902
No. observed reflections	2089	1074	2149
No. parameters	263	272	475
Weighting scheme	$1/\sigma^2(F_o)$	1	$1/\sigma^2(F_o)$
Maximum and average Δ/σ	0.028, 0.002	0.644, 0.017	1.11, 0.084
Maximum and minimum $\Delta\rho$/e Å^{-3}	+0.79, −0.78	+0.71, −0.62	+0.67, −1.03
S	2.22	3.29	2.37
R, R'	0.078, 0.049	0.072, 0.072	0.085, 0.056

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

L–Cu–L angle in planar three-co-ordinated copper(I) complexes CuL_3 is usually longer than the other two Cu–L bonds. When, on the other hand, one of the three L–Cu–L angles is less than 120° then the bond opposite is shorter than the others. The structural data presented here reveal excellent examples of this behaviour. Fig. 10 shows a graph of the difference, Δl, between the 'exceptional' Cu–N bond length and the average of the remaining two Cu–N bond lengths as a function of the difference, $\Delta\alpha$, between the corresponding 'exceptional' bond angle and the average of the remaining bond angles. For all the complexes, with the exception of **5**, both $\Delta\alpha$ and Δl are positive. All data presented here have been included, with the exception of those of **7**, where all three angles are essentially equal to 120° but where one bond length is apparently much greater than the others. The disorder of the anion has, however, produced exceptionally large errors in all three bond lengths and the difference between the longest and the shortest bond length is only just significant. Also included are the data for tris(2-methylpyridine)copper(I) perchlorate. The data have been fitted by the linear relationship (2).

Table 4 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for complexes **1**, **4**, **5**, **7**, **10**, **13** and **14**. For the PF_6 anions, only the coordinates of the P atom are reported

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Compound **1**							
Cu	0.231 7(1)	0.200 37(8)	0.233 20(7)	C(9)	0.323(2)	0.528(1)	0.243(1)
N(1)	0.243 7(7)	0.127 7(5)	0.131 6(5)	C(10)	0.189(2)	0.497 0(9)	0.213 2(9)
N(2)	0.278 5(9)	0.339 5(5)	0.235 9(4)	C(11)	0.168(1)	0.400 9(8)	0.210 0(7)
N(3)	0.172 6(9)	0.173 8(5)	0.337 8(5)	C(12)	0.529(1)	0.305 4(9)	0.296 6(7)
C(1)	0.180(1)	0.043 2(7)	0.108 0(6)	C(13)	0.243(1)	0.117 2(7)	0.401 8(7)
C(2)	0.199(1)	−0.005 7(7)	0.038 9(8)	C(14)	0.195(1)	0.098 8(8)	0.472 8(7)
C(3)	0.284(1)	0.030(1)	−0.007 8(7)	C(15)	0.073(2)	0.143(1)	0.479 0(7)
C(4)	0.347(1)	0.116 3(9)	0.013 0(7)	C(16)	0.000(1)	0.200 9(9)	0.414 7(8)
C(5)	0.325(1)	0.162 1(7)	0.083 5(7)	C(17)	0.055(1)	0.215 6(7)	0.346 5(6)
C(6)	0.091(1)	0.007 4(6)	0.162 9(6)	C(18)	0.377(1)	0.072 8(7)	0.393 6(6)
C(7)	0.412(1)	0.373 8(8)	0.266 6(6)	P	0.743 6(3)	0.223 0(2)	0.593 5(2)
C(8)	0.431(2)	0.468(1)	0.268 3(9)				
Compound **4**							
Cu(1)	0.586 0(2)	0.127 0(2)	0.747 2(1)	Cu(01)	0.791 5(2)	0.360 9(2)	0.294 9(1)
N(1)	0.743(1)	0.120 2(9)	0.821 9(9)	N(01)	0.752(1)	0.435 4(9)	0.413 9(8)
C(1)	0.745(2)	0.097(1)	0.899(1)	C(01)	0.683(2)	0.507(1)	0.429(1)
C(2)	0.859(2)	0.102(1)	0.953(1)	C(02)	0.667(2)	0.560(1)	0.513(1)
C(3)	0.969(2)	0.132(2)	0.925(2)	C(03)	0.720(2)	0.531(1)	0.585(1)
C(4)	0.966(2)	0.155(1)	0.848(2)	C(04)	0.786(2)	0.457(1)	0.572(1)
C(5)	0.855(2)	0.148(1)	0.800(1)	C(05)	0.802(2)	0.410(1)	0.486(1)
C(6)	0.617(2)	0.064(1)	0.921(1)	C(06)	0.628(2)	0.526(1)	0.345(1)
C(7)	0.856(3)	0.076(2)	1.039(1)	C(07)	0.597(2)	0.642(1)	0.531(1)
N(2)	0.553(1)	0.264 7(9)	0.786 2(8)	N(02)	0.817(1)	0.226 1(9)	0.291 6(8)
C(8)	0.455(2)	0.297(1)	0.830(1)	C(08)	0.931(2)	0.201(1)	0.316(1)
C(9)	0.442(2)	0.390(1)	0.860 1(9)	C(09)	0.938(2)	0.106(1)	0.304(1)
C(10)	0.535(2)	0.450(1)	0.843(1)	C(010)	0.833(3)	0.045(1)	0.269(2)
C(11)	0.634(2)	0.417(2)	0.796(1)	C(011)	0.722(2)	0.072(2)	0.243(1)
C(12)	0.638(2)	0.325(2)	0.768(1)	C(012)	0.718(2)	0.166(2)	0.257(1)
C(13)	0.364(2)	0.227(1)	0.848(1)	C(013)	1.039(2)	0.273(1)	0.351(1)
C(14)	0.333(2)	0.423(1)	0.911(1)	C(014)	1.060(2)	0.079(2)	0.331(1)
N(3)	0.464(1)	0.051 8(9)	0.644 6(8)	N(03)	0.805(1)	0.367 5(9)	0.170 1(9)
C(15)	0.468(2)	−0.039(1)	0.606(1)	C(015)	0.913(2)	0.393(1)	0.145(1)
C(16)	0.372(2)	−0.093(1)	0.538(1)	C(016)	0.925(2)	0.379(1)	0.055(1)
C(17)	0.274(2)	−0.048(1)	0.515(1)	C(017)	0.814(2)	0.341(1)	−0.006(1)
C(18)	0.270(2)	0.044(1)	0.553(1)	C(018)	0.703(2)	0.318(1)	0.021(1)
C(19)	0.368(2)	0.092(1)	0.616(1)	C(019)	0.703(2)	0.331(1)	0.111(1)
C(20)	0.579(2)	−0.081(1)	0.638(1)	C(020)	1.021(2)	0.441(1)	0.216(1)
C(21)	0.375(2)	−0.194(1)	0.497(1)	C(021)	1.050(2)	0.399(2)	0.024(1)
P(1)	0.328 7(5)	0.235 5(4)	0.143 6(4)	P(01)	0.053 1(5)	0.271 6(4)	0.638 2(4)
Compound **5**							
Cu	0	0.138 25(5)	0.528 4(2)	C(8)	0.163(1)	0.159 8(4)	0.349(2)
N(1)	0	0.132 4(4)	0.745(1)	C(9)	0.232(1)	0.153 1(4)	0.254(2)
C(1)	0	0.157 9(6)	0.845(3)	C(10)	0.258(1)	0.119 5(5)	0.219(2)
C(2)	0	0.151 0(7)	0.994(3)	C(11)	0.210(1)	0.091 4(4)	0.284(2)
C(3)	0	0.117 0(9)	1.045(3)	C(12)	0.141 0(9)	0.100 4(4)	0.378(1)
C(4)	0	0.089 0(7)	0.941(2)	C(13)	0.132(1)	0.195 4(4)	0.386(1)
C(5)	0	0.098 6(5)	0.796(2)	C(14)	0.236(1)	0.054 1(4)	0.252(2)
C(6)	0	0.195 2(6)	0.792(2)	P(1)	1/4	1/4	0
C(7)	0	0.051 4(6)	0.985(2)	P(2)	0	0	1/2
N(2)	0.113 3(7)	0.133 0(3)	0.409 9(9)				
Compound **7**							
Cu	0.261 3(3)	0	1/3	C(7)	0.547(1)	0.220(2)	0.312(1)
N(1)	0.370(1)	0.048(1)	0.231 5(9)	N(2)	0.087(2)	0	1/3
C(1)	0.331(2)	−0.021(1)	0.160(1)	C(8)	−0.016(2)	−0.097(2)	0.365(1)
C(2)	0.408(3)	0.014(3)	0.094(1)	C(9)	−0.138(3)	−0.102(2)	0.365(2)
C(3)	0.533(3)	0.103(3)	0.092(2)	C(10)	−0.137(4)	0	1/3
C(4)	0.581(2)	0.179(2)	0.165(2)	C(11)	−0.010(2)	−0.209(2)	0.399(1)
C(5)	0.499(2)	0.143(2)	0.233(1)	P	0.456 9(7)	0	5/6
C(6)	0.186(2)	−0.116(1)	0.163 6(8)				
Compound **10**							
Cu	0	1/4	−0.001 5(2)	N(01)	0.113 5(5)	1/4	0.104 3(8)
N(1)	0	1/4	−0.228(1)	C(01)	0.151 8(4)	0.188 0(3)	0.145 0(7)
C(1)	0	0.186 9(5)	−0.303 3(9)	C(02)	0.227 2(4)	0.185 2(4)	0.223 9(8)
C(2)	0	0.183 8(5)	−0.459 3(9)	C(03)	0.264 6(6)	1/4	0.265(1)
C(3)	0	1/4	−0.536(1)	C(04)	0.268 2(6)	0.114 3(4)	0.262(1)
C(4)	0	0.113 4(5)	−0.542(1)	P	0	0	0

Table 4 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Compound **13**			
Cu	0.115 96(9)	1/4	0.723 8(2)
N(1)	0.138 8(4)	0.361 8(6)	0.778(1)
C(1)	0.098 8(6)	0.412 4(9)	0.841(1)
C(2)	0.114 2(7)	0.492 3(9)	0.860(1)
C(3)	0.171 8(7)	0.520 7(8)	0.815(1)
C(4)	0.213 4(5)	0.469 0(7)	0.756(1)
C(5)	0.194 6(5)	0.389 8(7)	0.740(1)
C(6)	0.037 8(6)	0.379 1(8)	0.885(2)
C(7)	0.276 0(5)	0.494 1(7)	0.709(1)
C(8)	0.321 4(6)	0.497 1(8)	0.827(2)
C(9)	0.385 2(8)	0.521 6(9)	0.788(2)
C(10)	0.431 7(8)	0.522(1)	0.898(2)
N(01)	0.063 6(7)	1/4	0.544(2)
C(01)	0.093(1)	1/4	0.419(3)
C(02)	0.059(1)	1/4	0.297(3)
C(03)	−0.002(1)	1/4	0.301(3)
C(04)*	−0.033(1)	0.274(3)	0.428(3)
C(05)	0.003 4(9)	1/4	0.540(2)
C(06)	0.162(1)	1/4	0.419(2)
C(07)*	−0.102(2)	0.288(3)	0.446(6)
C(08)*	−0.139(2)	0.211(3)	0.425(5)
C(09)*	−0.213(3)	0.204(4)	0.434(8)
C(010)*	−0.238(3)	0.273(2)	0.468(7)
P	0.863 1(3)	1/4	0.937 0(7)
Compound **14**			
Cu(1)	0.127 8(1)	0.336 8(3)	0.366 8(1)
N(1)	0.041 2(8)	0.251(2)	0.354(1)
C(1)	−0.008(1)	0.295(2)	0.313(1)
C(2)	−0.069(1)	0.237(3)	0.303(2)
C(3)	−0.070(1)	0.136(2)	0.342(2)
C(4)	−0.016(1)	0.100(2)	0.381(1)
C(5)	0.040(1)	0.157(2)	0.391(1)
C(6)	−0.007(1)	0.408(3)	0.277(2)
C(7)	−0.137(2)	0.077(3)	0.332(2)
C(8)	0.095(1)	0.110(2)	0.437(1)
N(2)	0.190 7(8)	0.351(2)	0.466 6(9)
C(9)	0.166(1)	0.399(2)	0.529(1)
C(10)	0.207(1)	0.416(2)	0.597(2)
C(11)	0.273(1)	0.390(2)	0.602(1)
C(12)	0.296 1(8)	0.342(2)	0.541(1)
C(13)	0.253 9(9)	0.318(2)	0.476(1)
C(14)	0.091(1)	0.426(2)	0.519(1)
C(15)	0.316(1)	0.412(2)	0.674(1)
C(16)	0.273 2(8)	0.268(2)	0.406(1)
N(3)	0.162 3(7)	0.410(2)	0.275(1)
C(17)	0.169(1)	0.523(2)	0.274(1)
C(18)	0.195(1)	0.574(2)	0.217(1)
C(19)	0.217(1)	0.507(3)	0.159(1)
C(20)	0.205(1)	0.399(2)	0.157(1)
C(21)	0.177 6(9)	0.353(2)	0.216(1)
C(22)	0.150(1)	0.586(2)	0.346(1)
C(23)	0.250(2)	0.561(3)	0.097(1)
C(24)	0.160(1)	0.225(2)	0.217(1)
Cu(01)	0	0	0
N(01)	−0.035 6(8)	−0.086(1)	0.082(1)
C(01)	−0.010 5(9)	−0.070(2)	0.158(1)
C(02)	−0.034(1)	−0.134(2)	0.215(1)
C(03)	−0.078(1)	−0.213(2)	0.202(1)
C(04)	−0.103(1)	−0.231(2)	0.125(2)
C(05)	−0.080 4(9)	−0.169(2)	0.067(1)
C(06)	0.037(1)	0.022(2)	0.174(1)
C(07)	−0.108(2)	−0.277(2)	0.260(1)
C(08)	−0.104 7(8)	−0.190(2)	−0.017(1)
N(02)	0	0.167(2)	0
C(09)	0.056(1)	0.222(2)	−0.005(1)
C(010)	0.055(1)	0.332(3)	−0.008(2)
C(011)	0	0.388(4)	0
C(012)	0.115 7(9)	0.158(2)	−0.014(2
C(013)	0	0.516(6)	0
P(1)	0.785 6(4)	0.441 1(8)	0.137 2(4)
P(01)	0	0.763(1)	1/2

* Atomic site refined with a population parameter of 0.5.

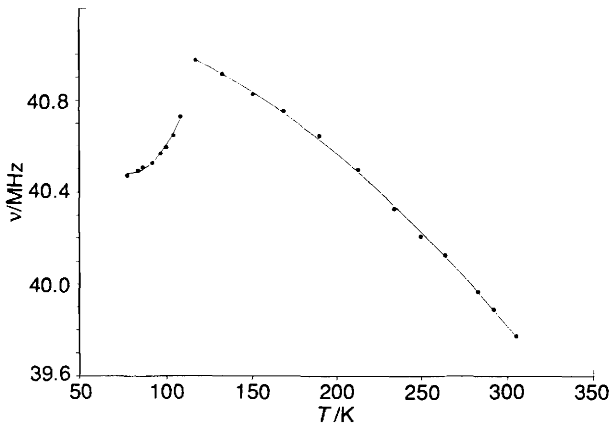

Fig. 9 The temperature dependence of the ^{63}Cu NQR frequencies of complex **10**

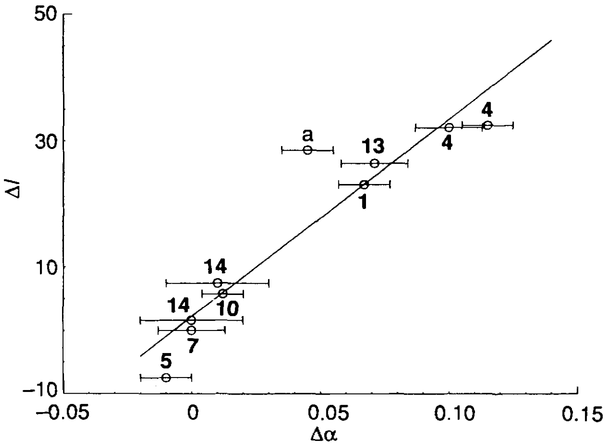

Fig. 10 The relationship between the difference, Δ*l*, between the 'exceptional' Cu–N bond length and the average of the remaining two Cu–N bond lengths and the difference, Δα, between the corresponding 'exceptional' bond angle and the average of the remaining bond angles. The point marked a corresponds to tris(2-methylpyridine)copper(I) perchlorate

$$\Delta l = -0.005\,25 + 0.002\,98\Delta\alpha;\quad \text{correlation coefficient } 0.889 \qquad (2)$$

Complex **10** is distinguished from the others by the fact that it is the only one where the co-ordinated pyridines are not substituted in position 2. This allows the copper atom to be doubly co-ordinated at axial positions by the PF_6 anion [shorter observed distance Cu···F: 3.004(4) Å] without influencing the orientation of the pyridine ligands (all dihedral angles 90°). The two co-ordinated fluorine atoms are well localised whereas the others are disordered (12 observed sites) in a plane perpendicular to the Cu–F bond (Fig. 4). The molecular packing is formed of chains ···Cu···F–P–F···Cu··· parallel to the *b* axis.

NQR Frequencies.—Both ^{63}Cu and ^{65}Cu have spins $I = \frac{3}{2}$ so

Table 5 Selected geometrical parameters of three-co-ordinated copper(I) complexes[a]

Compound	(asym. unit)	**1**	**4**	**5**	**7**	**10**	**13**	**14**
Ligand		2-Methylpyridine	2,3-Dimethylpyridine	2,5-Dimethylpyridine	2,6-Dimethylpyridine	3,5-Dimethylpyridine	5-Butyl-2-methyl pyridine	2,4,6-Trimethylpyridine
PF_6 Anion		Ordered	Disordered	Disordered	Disordered	Disordered	Disordered	Ordered
Symmetry of CuL_3[b]	(1)	General	General	m	C_2	$2\perp m + C_2$	m	General
	(2)		General					C_2
Cu–N/Å	(1)	1.962(4)	1.97(1)	1.96(1)	2.00(1)	1.991(7)	1.979(9)	2.04(2)
		1.964(9)	1.98(1)	1.981(9)	2.00(1)	1.991(7)	1.979(9)	2.04(2)
		2.030(7)	2.09(1)	1.981(9)	2.05(2)	2.003(9)	2.05(2)	2.05(2)
	(2)		1.99(1)					2.01(2)
			2.01(1)					2.01(2)
			2.10(2)					2.01(2)
N–Cu–N/°	(1)	135.3(3)	141.5(5)	121.4(3)	120(1)	123.8(3)	137.7(4)	124.9(8)
		106.8(3)	112.1(5)	121.4(3)	120.1(5)	118.1(2)	110.8(3)	121.8(7)
		117.7(3)	106.1(5)	113.9(4)	120.1(5)	118.1(2)	110.8(3)	113.2(7)
	(2)		141.3(6)					121.1(5)
			112.1(6)					121.1(5)
			106.4(5)					117.9(7)
ΔCu/Å[c]	(1)	0.036(1)	0.061(3)	0.206(8)	0	0	0.095(6)	0.037(5)
	(2)		0.046(3)					0
φ[d]/°	(1)	64.9(4)	4.1(5)	90	58.2(9)	90	103.3(4)	42.3(9)
		18.8(4)	82.4(7)	89.6(6)	58.2(9)	90	103.3(4)	56.0(8)
		82.7(4)	69.3(6)	90.4(6)	46.6(8)	90	90	65.1(7)
	(2)		26.4(6)					54.3(4)
			97.8(6)					54.3(4)
			96.2(6)					51.6(5)
Minimum Cu ··· F distance/Å		3.356(6)	3.68(3)	3.68(3)	4.82(2)	3.004(4)	3.98(6)	5.08(2)

[a] The bond lengths Cu–N are arbitrarily reported in the increasing order ($a < b < c$). Thus the N–Cu–N bond angles (ab, ac, bc) and dihedral angles (φa, φb, φc) are given with respect to this order. [b] General, no symmetry; C_2, two-fold axis; m, mirror plane. [c] Distances Cu from plane of the three co-ordinated N atoms. [d] Dihedral angle between the mean plane of the substituted pyridine rings and the plane of the three co-ordinated N atoms.

that the resonance frequencies are related to the coupling constant, e^2Qq_{zz}, and the asymmetry parameter, η, by relationship (3) where the asymmetry parameters is defined as in

$$\nu = \frac{e^2Qz_{zz}}{2}\left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \tag{3}$$

equation (4). It is only possible to separate the two terms in this

$$\eta = (q_{xx} - q_{yy})/q_{zz} \tag{4}$$

equation [(3)] by means of Zeeman measurements on large single crystals; this we have so far been unable to do. However the effect of the asymmetry parameter on the resonance frequency is negligible compared with that of the coupling constant, even for an asymmetry parameter as great as 0.5. The coupling constant is therefore approximately equal to twice the resonance frequency.

The resonance frequencies of the analogous two-co-ordinated cations lie between 39 and 42 MHz and it proved possible to correlate this spread in frequency with the lengths of the Cu–N bonds,[2] but for these three-co-ordinated species there does not appear to be any notable correlation between the structural and the NQR data with the exception of the data for **10** discussed below. The partial field-gradient model for the coupling constants of poly-co-ordinated nuclei[10] implies that the field-gradient z axis lies perpendicular to the trigonal plane formed by the copper atom and the three nitrogen atoms and, provided that the same partial field gradient can be assigned to the pyridine ligand in both the two- and the three-co-ordinated species, that the magnitude of the field gradient of the three-co-ordinated complexes is three-quarters of that of the two-co-ordinate complexes. This is clearly not the case. A similar, though much less-marked, behaviour was observed for two- and three-co-ordinated copper(I) polyhalide anions[11] while for two- and three-co-ordinated gold(I) complexes the quadrupole splittings of the ^{197}Au Mössbauer spectra are approximately the same for both co-ordination numbers.[12]

A description of the bonding in the two- and three-co-ordinated complexes in terms of the 3d and 4p orbitals leads to the creation of a hole in the 3d shell, producing a positive field gradient, and an electron density in the 4p shell, producing a negative field gradient. The resulting field gradient arises therefore from the difference of two similar terms. Consequently small changes in the relative contributions of the 3d hole and the 4p electron density produces large changes in the field gradient. The difficulty is exacerbated by the fact that there is theoretical evidence that the radial wavefunctions of the 3d and 4p electrons change markedly with co-ordination number.[13,14] It must be stressed, however, that we are for the moment ignorant of the asymmetry parameters and of the directions of the field-gradient axes in both sets of complexes, so further speculation as to the cause of this behaviour must await the availability of these data.

With the exception of complexes **3**, **10** and **12** the resonance frequencies at 77 K all lie between 44 and 47 MHz. The resonance signal of **12** fades out below 244 K but its extrapolated frequency at 77 K is 44.9 MHz; it therefore does not constitute an exception. Of the remaining two complexes the resonance of **10** is by far the most 'abnormal'. With the exception of **10**, the temperature dependence of the NQR frequencies of the three-co-ordinated cations is markedly different from that of the two-co-ordinated cations. The frequencies of the latter group decrease by around 1.0 MHz on going from 77 K to room temperature whereas for the three-co-ordinated complexes the change is three times as great. A convenient measure of the temperature dependence is the slope of the frequency *vs.* temperature curve at some fixed temperature. Table 6 shows this term measured at 300 K; the slopes are centred around −15 kHz K^{-1}; for the two-co-ordinated cations a typical value is −5 kHz K^{-1}.

Table 6 Copper-63 NQR frequencies of three-co-ordinated copper(I) cationic complexes $[CuL_3]X$, measured at 77 K, together with their temperature dependences. In all cases ^{65}Cu resonances were observed at a frequency 0.925 times that of the ^{63}Cu isotope

Ligand	Anion	ν_{77}/MHz	ν_0/MHz	A/kHz K^{-1}	B/Hz K^{-2}	$(d\nu/dT)_{300}$/ kHz K^{-1}
2-Methylpyridine	PF_6	44.728	45.096	−3.455	−14.347	−12.06
2-Ethylpyridine	ClO_4	45.450	46.385	−10.345	−8.055	−15.18
2-Benzylpyridine	PF_6	42.800	43.220	−4.566	−11.677	−11.57
2,3-Dimethylpyridine	PF_6	46.892 44.900	47.629	−8.512	−12.996	−16.31
2,5-Dimethylpyridine	ClO_4	44.848	46.257	−10.322	−9.119	−17.50
	PF_6	45.474 44.906	45.526[a]	−4.474	−21.703	−15.80
2,6-Dimethylpyridine	PF_6	45.584 45.124 44.607	45.407[b]	−7.641	−11.302	−14.42
	ClO_4	44.554[c] 44.293[c]	45.164	−4.815	−17.516	−15.32
	BF_4	44.660	45.187	−5.174	−15.841	−14.68
		44.291	44.717	−3.916	−16.382	−13.75
		44.263	44.730	−4.694	−13.583	−12.84
3,5-Dimethylpyridine	PF_6	40.471	41.219[d]	−0.428	−14.159	−8.92
5-Ethyl-2-methylpyridine	PF_6	45.710	46.122	−3.525	−23.147	−17.41
	ClO_4	43.219[e]	45.169[f]	−1.533	−28.986	−18.92
5-Butyl-2-methylpyridine	PF_6	44.556	45.244	−7.200	−13.807	−15.48
2,4,6-Trimethylpyridine	PF_6	44.832	45.633	−3.886	−15.617	−13.26
		44.770	45.661	−5.117	−11.487	−12.01
		44.592	45.542	−5.617	−12.012	−12.82

[a] For the temperature range after the phase transition; 100–305 K. [b] For the temperature range after the phase transition; 155–305 K. [c] At 92.4 K. [d] For the temperature range after the phase transition; 117–305 K. [e] At 244 K. The resonance disappears below this temperature. [f] For the temperature range 249–307 K.

For complex **10** both the resonance frequency and its temperature dependence are significantly different from those of the other complexes. There is little doubt that this is associated with the co-ordination to the PF_6 anion. A similar behaviour was noted[1] for both the resonance frequency and temperature dependence of bis(2,6-dimethylpyridine)copper(I) nitrate, where the structural parameters[15] also militate in favour of cation–anion co-ordination. Thus, provided that the partial field gradient of a weakly co-ordinated anion is of the same sign as that of the pyridine ligand, an axial co-ordination to the anion decreases the resonance frequency, while this additional co-ordination will lock the copper atom more tightly to the crystal lattice and thus, by decreasing its mobility, decrease the temperature dependence of the resonance frequency. Of the remaining complexes it is noteworthy that the temperature dependence of **1**, where we have structural evidence for weak anion co-ordination, and of **3**, where structural information is absent but where the NQR frequency is low, is intermediate between the −15 kHz K^{-1} of the other complexes and the −8 kHz K^{-1} of **10**. On the other hand, because, on the evidence of the Cu···F interatomic distance, the co-ordination to the anion is weaker in **1** than in **10**, the resonance frequency of **1** is not markedly different from those of the majority of the three-co-ordinated complexes.

Conclusion

The crystal structures of these three-co-ordinated copper(I) cations are in the main determined by intermolecular interactions between the pyridine ligands. The ^{63}Cu NQR frequencies of these cations are notably higher than those of the corresponding two-co-ordinated species, and these frequencies are likewise much more temperature-dependent. When the ligand has no hindering substituent in the 2 position, both the structural parameters and the NQR frequencies show clear evidence for co-ordination between the copper cation and the anion.

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References

1 A. Habiyakare and E. A. C. Lucken, *Z. Naturforsch., Teil A*, 1989, **45**, 224.
2 A. Habiyakare, E. A. C. Lucken and G. Bernardinelli, *J. Chem. Soc., Dalton Trans.*, 1991, 2269.
3 A. H. Lewin, R. J. Michl, P. Ganis and U. Lepore, *J. Chem. Soc., Chem. Commun.*, 1972, 661.
4 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York and Louvain-la-Neuve, 1987.
5 S. R. Hall and J. M. Stewart (editors), *XTAL User's Manual*, Universities of Western Australia and Maryland, 1989.
6 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
7 D. Schwarzenbach, S. C. Abrahams, H. D. Flack, W. Gonschorek, Th. Hahn, K. Huml, R. E. Marsh, E. Prince, B. E. Robertson, J. S. Rollett and A. J. C. Wilson, *Acta Crystagllogr., Sect. A*, 1989, **45**, 63.
8 G. Bernardinelli and H. D. Flack, *Acta Crystallogr., Sect. A*, 1985, **41**, 500.
9 J. F. Riehl, I. El-Idrissi Rachidi, Y. Jean and M. Pelissier, *New J. Chem.*, 1991, **15**, 239.
10 T. B. Brill, in *Advances in Nuclear Quadrupole Resonance*, vol. 3, ed. J. A. S. Smith, Academic Press, London, New York, 1978.
11 S. Ramaprabhu and E. A. C. Lucken, *J. Chem. Soc., Dalton Trans.*, 1991, 2615.
12 R. V. Parish, in *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, ed. G. J. Long, Plenum, New York, 1984, vol. 1, p. 577.
13 G. A. Bowmaker and P. D. W. Boyd, *J. Mol. Struct.*, 1985, **122**, 299.
14 G. A. Bowmaker, P. D. W. Boyd and R. J. Sorrenson, *J. Chem. Soc., Faraday Trans.*, 1985, 1023.
15 L. M. Engelhardt, C. Packawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 117.

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