The ^{63,65}Cu NQR Spectra of Di-coordinated Cu^I Cations with 2-Substituted Pyridine Ligands*

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The NQR frequencies of the ^{63,65}Cu nuclei in di-coordinated complex cations of Cu^I, having the general formula CuL$_2$X, where L is a substituted pyridine and X is a hard anion such as ClO$_4$, are reported and discussed in the light of the known crystal structures. A departure from a strictly linear geometry of the L$_2$Cu cation has but little effect on the resonance frequency, but the donor-acceptor bond between the nitrate anion and the copper atom in bis(2,6-lutidine)cuprous nitrate, which was postulated on crystallographic grounds, is confirmed by the NQR results, which also indicate a similar interaction in bis(2,6-lutidine)cuprous trifluoroacetate. A number of the complexes discussed here have not been reported previously.

Introduction

The preferred configuration of Cu^I is tetrahedral tetracoordination but with bulky, sterically-hindered ligands lower coordination numbers are readily obtainable. As we [1] and others [2, 3] have shown, the ^{63,65}Cu NQR resonance frequencies of such complexes are highly dependent on the coordination number. Thus the complexes $(L_2X)_n$ of cuprous halides with phosphine [2, 3] or pyridine [1] ligands may be tricoordinated and monomeric, showing a ^{63}Cu NQR frequency around 35 MHz, or be tetracoordinated halogen-bridged dimers showing a ^{63}Cu NQR frequency around 15 MHz.

If, instead of a halide, the anion is a poorly coordinating species such as ClO_4^-, then sterically-hindered ligands such as 2,6-lutidine give rise to complex cations L_2Cu^+ with an approximately linear geometry, the crystal-structure of several such species having been determined [4]. With NO_3^- as anion, however, although the approximately linear geometry for the cation is maintained, there is some evidence from bond-distances that the interaction between the nitrate anion and the copper anion is by no means negligible so that the copper atom may be more correctly considered to be in a higher coordinated environment [4]. We have therefore undertaken a systematic study of complexes of hindered pyridine ligands with a variety of cations, hoping that these studies may throw more light on the details of the electronic structure of these complexes.

Experimental

Preparations

Table 1 shows a list of all compounds studied here, together with their elemental analyses which were performed by the Geneva University Microanalytical Laboratory (Dr. H. Eder). Compounds **1**–**4** and **8**–**17** were prepared by reducing solutions of the corresponding cupric salt and the ligand in a 1 : 2 molar ratio in boiling aqueous ethanol with ascorbic acid. The resulting solutions were filtered while hot and the corresponding complexes crystallised out on cooling. Compounds **5**–**7** were prepared by a similar reduction of cupric sulphate followed by addition of an excess of, respectively, potassium hexafluorophosphate, chlorate or trifluoroacetate to the warm solution in ethanol. This method of preparation yields the non-linear polymorph, (b), of bis(2,6-lutidine)cuprous perchlorate [5]; the linear polymorph, (a), [4], was prepared by dissolving the β-polymorph in acetonitrile containing a large excess of 2,6-lutidine and slowly recrystallising the desired complex by vapour diffusion of diethylether into the solution. The complexes were further characterised by their IR-spectra, measured on a Mattson Polaris FTIR spectrometer in 4000–400 cm^{-1}. The presence of bands characteristic of both the ligand and the anion was observed in all cases.

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Table 1. Elemental analyses of the complexes CuL_2X. Figures in parentheses are theoretical values.

No.	Ligand (L)	Anion (X)	C	H	N
1	2,6-lutidine	ClO_4	44.47 (44.57)	4.77 (4.81)	7.35 (7.42)
2	2,6-lutidine	BF_4	45.96 (46.11)	4.93 (4.97)	7.52 (7.68)
3	2,6-lutidine	NO_3	49.18 (49.47)	5.23 (5.34)	12.19 (12.36)
4	2,6-lutidine	CF_3SO_3	41.48 (42.20)	4.20 (4.25)	6.31 (6.56)
5	2,6-lutidine	PF_6	39.70 (39.77)	4.26 (4.29)	6.61 (6.62)
6	2,6-lutidine	ClO_3	46.43 (46.54)	5.00 (5.02)	7.67 (7.75)
7	2,6-lutidine	CF_3CO_2	48.25 (49.17)	4.50 (4.64)	7.02 (7.17)
8	2,4-lutidine	ClO_4	44.43 (44.57)	4.78 (4.81)	7.36 (7.42)
9	2,5-lutidine	ClO_4	44.47 (44.57)	4.78 (4.81)	7.38 (7.42)
10	2,4,6-collidine	ClO_4	47.43 (47.40)	5.39 (5.47)	6.88 (6.91)
11	2,4,6-collidine	BF_4	48.83 (48.94)	5.55 (5.65)	7.09 (7.13)
12	2,4,6-collidine	CF_3SO_3	44.57 (44.87)	4.52 (4.87)	6.01 (6.15)
13	2,6-diphenyl pyridine	ClO_4	65.07 (65.28)	4.19 (4.19)	4.43 (4.48)
14	2,6-diphenyl pyridine	BF_4	66.64 (66.63)	4.25 (4.28)	4.57 (4.57)
15	2,6-dimethoxy pyridine	ClO_4	38.07 (38.11)	4.07 (4.11)	6.30 (6.35)
16	2,6-dimethoxy pyridine	BF_4	39.08 (39.23)	4.17 (4.23)	6.46 (6.54)
17	2,6-dimethoxy pyridine	CF_3SO_3	36.27 (36.70)	3.59 (3.70)	5.63 (5.71)

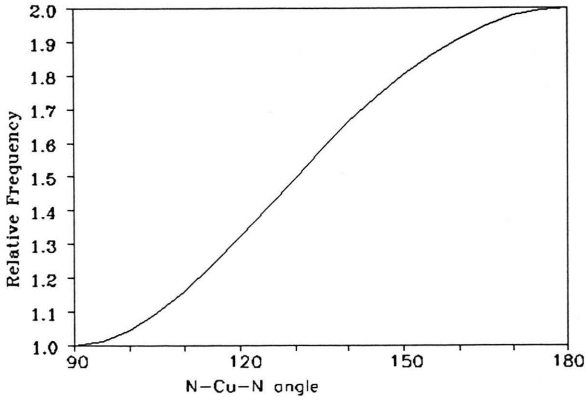

Fig. 1. Angular dependence of the NQR frequency of a central spin 3/2 nucleus of a dicoordinated L-M-L species as a function of the L-M-L angle, predicted by the partial field-gradient model.

NQR Spectra

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.

Results and Discussion

The ^{63,65}Cu NQR frequencies are shown in Table 2. The temperature dependence of the resonance frequencies was determined at 77–300 K and the results fitted to a second order polynomial

$$f = f_0 + AT + BT^2 .$$

The values of these parameters are also given in Table 2.

This study was initiated on the working hypothesis, based on the partial field-gradient model for polycoordinated complexes [6], that the frequency of a linear complex would be greater than that of a non-linear one. For a spin 3/2 nucleus such as we have here, this theory indicates a smooth sigmoid relationship for the relative resonance frequency as the bond-angle varies from 90° to 180° (Figure 1). The first two complexes studied, bis(2,6-lutidine)cuprous perchlorate and nitrate, (**1 b, 3**), seemed to provide a striking confirmation of this hypothesis but the perchlorate of the 2,4-lutidine complex, (**8**), shown by X-ray crystallography to be non-linear, has a resonance frequency not only not smaller than that of the 2,6-lutidine perchlorate but suspiciously similar to it. This similarity led us to verify their identity carefully by, inter alia, measuring their crystallographic parameters. These, while confirming the identity of the complex of 2,4-lutidine, demonstrated that the complex of 2,6-lutidine was not the same as previously reported [4]. The existence of a second isomorph of bis(2,6-lutidine)cuprous perchlorate, having the same crystallographic parameters as the complex we had prepared, in which the complex cation is non-linear and non-planar, has been reported shortly afterwards [5], and we were able to convert this isomorph to the linear complex by recrystallisation from a mixture of acetonitrile and 2,6-lutidine. The measurement of the resonance frequency of the linear planar complex, by 1.5 MHz smaller than that of the non-planar non-linear variety, provoked

Table 2. ^{63,65}Cu NQR frequencies of CuL_2^+ cations and their temperature dependence. The compounds are identified by the numbers in the first column which refer to their explicit identification in Table 1.

	Frequency (MHz at 77 K)		Temperature dependence (^{63}Cu)			$(df/dT)_{300}$
	^{63}Cu	^{65}Cu	f_0 (MHz)	A (kHz K^{-1})	B (Hz K^{-2})	(kHz K^{-1})
1a	39.400	36.461	39.640	−2.226	−6.306	−6.01
1b	40.892	37.860	41.126	−2.303	−3.758	−4.56
2	41.275	38.200	41.498	−2.422	−3.626	−4.60
3	32.650	30.212	32.748	−1.348	1.957	−0.17
4	39.220	36.297	39.554	−3.627	−4.890	−6.56
5	41.951	38.829	42.149	−1.778	−7.221	−6.11
6	37.041	34.293	37.400	−3.733	−7.896	−8.47
	27.780 *	21.900 *	27.928	4.806	−84.334	−45.79
7	33.255	30.781	33.848	−8.034	9.303	−2.45
8	40.867	37.820	41.056	−1.949	−5.319	−5.14
9	40.558	37.533	40.759	−2.100	−7.599	−6.66
10	41.075	38.012	41.707	−8.314	6.658	−4.37
	40.956	38.911	41.484	−6.286	2.187	−4.97
	40.957	37.912	41.418	−5.718	1.015	−5.11
	40.862	37.825	41.200	−3.856	−2.812	−5.54
11	41.17 **	38.10 **	41.470	−2.837	−4.715	−5.66
12	37.850	35.025	38.171	−3.341	−5.204	−6.46
13	40.285	37.286	40.505	−2.168	−7.847	−6.87
14	40.265	37.264	40.496	−2.342	−7.153	−6.63
15	39.206	36.282	39.310	−3.506	−11.287	−7.12
	38.321	35.482	38.350	−13.035	− 5.660	−3.53
16	39.325	36.381	39.490	−1.487	−10.935	−8.05
	38.589	35.692	38.516	1.461	−11.364	−5.36
17	39.750	36.745	39.963	−1.974	−9.851	−7.88

* ^{35,37}Cl frequencies. – ** Measured at 104 K; the resonances are undetectable at 77 K.

the rapid demise of the working hypothesis and induced the more extensive study reported here.

The initial problem was thus to explain the lower frequency of the linear planar isomorph of the perchlorate. Fortunately, the crystallographic parameters of the two complexes provide an immediate answer. Presumably owing to repulsive interactions between the methyl groups, the Cu–N distance in the planar isomorph is 1.936(5) Å [4] while it is 1.879(16) Å and 1.953(22) in the non-planar form. The shorter bond length – and consequently greater deformation of the spherically-symmetric isolated Cu$^+$ cation – is certainly responsible for the higher resonance frequency of the non-planar isomorph.

With the abandonement of the initial hypothesis, the low resonance frequency of the nitrate must be ascribed to complexation with the nitrate anion. The frequency of the nitrate may be compared to that of the three-coordinated complexes of 2,6-lutidine with the cuprous halides, L_2CuX (38.32, 37.60 and 36.96 MHz for X=Cl, Br and I, respectively) or the four-coordinated halogen-bridged dimers of 2-picoline, (L_2CuX), where the frequencies lie around 15 MHz [1]. The resonance frequencies of complexes with the well-known hard anions perchlorate, tetrafluoborate and hexafluorophosphate are all very similar, and all have a similar temperature dependence (Fig. 2), with the usual negative values of the coefficients A and B. By contrast, the temperature dependence of the nitrate is quite different (Fig. 3), with A and B of opposing

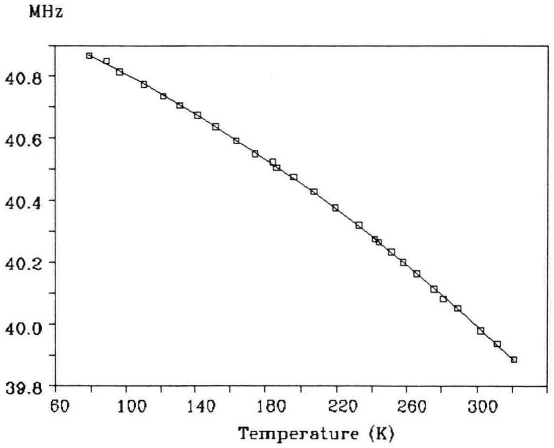

Fig. 2. Temperature dependence of the ^{63}Cu NQR frequency of bis(2,4-lutidine)cuprous perchlorate.

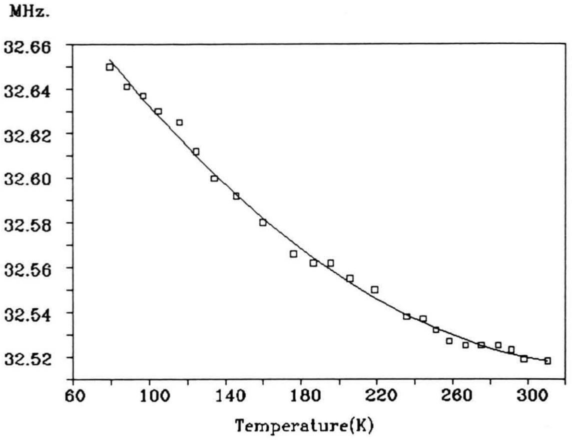

Fig. 3. Temperature dependence of the ^{63}Cu NQR frequency of bis(2,6-lutidine)cuprous nitrate.

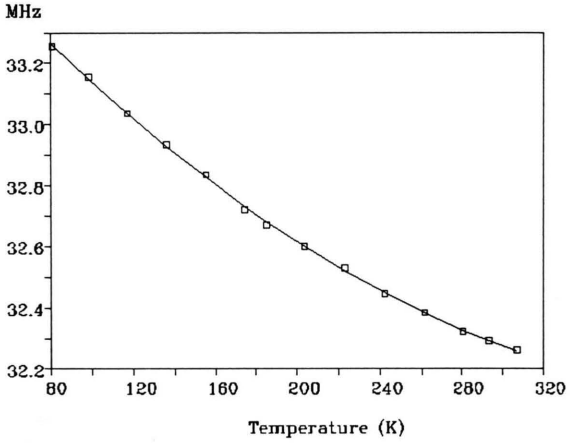

Fig. 4. Temperature dependence of the ^{63}Cu NQR frequency of bis(2,6-lutidine)cuprous trifluoroacetate.

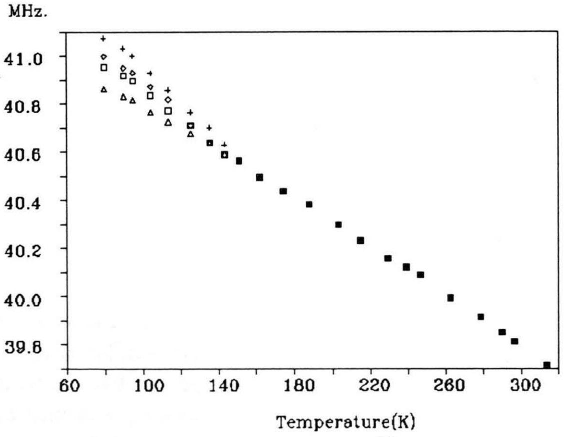

Fig. 5. Temperature dependence of the ^{63}Cu NQR frequency of bis(2,4,6-collidine)cuprous perchlorate.

Table 3. Structural parameters of CuL_2X complexes.

Ligand	Anion	Angles		Length	Ref.
		N–Cu–N	Dihedral	Cu–N	
2,6-lutidine (**1a**)	ClO_4	180	0	1.936	[4]
2,6-lutidine (**1b**)	ClO_4	171	56	1.879 1.953	[5]
2,6-lutidine	NO_3	166	0	1.966 1.956	[4]
2,6-lutidine	BF_4	173	64	1.900	[7]
2,4-lutidine	ClO_4	170	51	1.86	[4]
2,4,6-collidine	BF_4	175	59	1.904	[7]
2,6-diphenyl-pyridine	ClO_4	158	55	1.95	[7]

signs, so that the change of frequency between 77 and 300 K is only 130 kHz compared to the 1 MHz of the complexes of the harder anions. The NQR results thus strongly support the conclusions of the crystallographic study [4] which argued for a strong interaction between the nitrate anion and the copper cation on the basis of a long N–O distance and a long Cu–N distance (1.966 Å).

The geometry of the complex copper cation in the nitrate is linear and planar. This planarity is essential if the nitrate is to have access to the copper cation, but in view of the demonstrated steric interaction between the methyl groups in the planar 2,6-lutidine complex, it is to be anticipated that the normal configuration with hard non-complexing anions will be non-planar. To test this hypothesis we have determined the structure of the perfluoborates of the 2,6-lutidine and 2,4,6-collidine complexes (**3**, **7**) and the perchlorate of the 2,6-diphenylpyridine complex (**8**) by X-ray crystallography [7]. In all cases the complexes are non-planar and non-linear. The results, together with those of the previously-reported determinations, as shown in Table 3. Purely steric considerations indicate in any case that the 2,6-diphenylpyridine complex cannot be planar; the X-ray structure not only confirms this but shows the smallest N–Cu–N angle of all the complexes studied. The essentially complete lack of the effect of this considerable bending on the resonance frequency completes the demonstration of the inapplicability of our initial working hypothesis.

Of all the other bis(2,6-lutidine)copper salts only one, the trifluoroacetate (**7**), has a frequency as low as that of the nitrate. Although its temperature dependence is considerable, the frequency at room temperature being by 1.0 MHz smaller than that at 77 K, the form of the temperature dependence is similar to that of the nitrate (Figure 4). Although we do not have, as yet, any crystallographic evidence of this, it is very likely that the trifluoroacetate ion must be considered to be a ligand of the copper cation. The trifluorosulphonate is, not surprisingly, similar to the complexes of the three-mentioned hard anions while only the chlorate exhibits an intermediate behaviour whose explanation must await further study by other physical methods.

Two of the complexes **10** and **11** of 2,4,6-collidine have temperature dependences which are indicative of motional effects, which are no doubt associated with the mobility of the highly-symmetrical cations. Thus the resonances of the perfluoborate are undetectable at 77 K and only appear at around 100 K while at 77 K the perchlorate shows four resonances which gradually merge into a single one around 150 K (Figure 5). We have been able to demonstrate such a motion directly in the case of the chlorate **6**, where the ^{35}Cl resonance fades out at 140 K following an unusually steep negative temperature dependence. Finally, all three complexes whose structures have been determined by us showed evidence of either structural or motional disorder [7].

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