The Nuclear Quadrupole Resonance of the ^{63,65}Cu Nuclei in Copper(I) Complexes*

Edwin A. C. Lucken

Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet, 1211 Genève 4, Switzerland

Z. Naturforsch. **49a**, 155–166 (1994); received August 23, 1993

The ^{63}Cu NQR spectra of Cu(I) complexes are surveyed and discussed in terms of the coordination number of the copper atom, the nature of the ligands and the charge of the complex.

Introduction

The Importance of Copper and Copper (I) Compounds

Copper(I) occurs in a variety of systems of current interest. It is present in high-temperature superconductors, but in addition the complexes of Cu(I) are important reagents in synthetic organic chemistry, they have interesting photochemical properties, and Cu(I) is an essential constituent of a number of enzymes. Twenty years ago our knowledge of the chemistry of divalent copper, Cu(II), was far more extensive than that of Cu(I) but recently there has been a rapid development in our knowledge of the Cu(I) chemistry, which has turned out to be particularly versatile.

The ^{63}Cu and the ^{65}Cu Nuclei

Table 1 shows the properties of the two naturally-occurring isotopes of copper, ^{63}Cu and ^{65}Cu. Both nuclei have spins of 3/2 and have similar quadrupole moments, but since ^{63}Cu has the higher abundance and the higher quadrupole moment, data will be quoted for this nucleus only. However both resonances can always be observed, a fact that is of much practical importance when systems containing several different quadrupolar nuclei are under study since it permits an unambiguous assignment of the resonance frequencies to the copper nuclei.

Since the spin of both isotopes is 3/2 there is only one resonance frequency for each of them, given by the relationship:

$$\nu_Q = \frac{e^2 Q q}{2}\sqrt{1+\frac{\eta^2}{3}}.$$

It is only possible to separate $e^2 Q q$ and η by Zeeman measurements, preferably on single crystals of known structure since only this method yields the orientation of the field-gradient tensor with respect to the molecular framework. This is particularly important for polycoordinated molecules such as the complexes of copper where there are often no clear *a priori* guide-lines as to this orientation. Relatively few Zeeman measurements of this kind are available (see Table 9 below), so that usually the asymmetry parameter is unknown but, even for an asymmetry parameter as high as 0.5, the error in equating the coupling constant to twice the resonance frequency is only 4%.

The Complexes of Cu(I)

The Ligands

A fairly recent survey of the chemistry of monovalent copper has been given by Hathaway [1]. The Cu(I) cation is highly polarisable; to the chemist it is a typical "soft" acceptor that forms its strongest com-

Table 1. The nuclear properties of the naturally-occuring isotopes of copper.

Isotope	Abundance (%)	Spin	Magnetic moment (Nuclear magnetons)	Quadrupole moment (barns)
63	69.09	3/2	2.2206	−0.220
65	30.91	3/2	2.3790	−0.204

The quadrupole coupling constant ratio ^{63}Cu/^{65}Cu is 1.085

* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance, Zürich, July 19–23, 1993.

Reprint requests to Prof. E. A. C. Lucken, Phys. Chem. Dept., Sciences II; University of Geneva; 30 Quai Ernest-Ansermet; 1211 Geneva 4; Switzerland.

0932-0784 / 94 / 0100-0155 $ 01.30/0. – Please order a reprint rather than making your own copy.

plexes with soft donors such as phosphorus, sulphur or iodine and its weakest complexes with hard donors such as oxygen or fluorine. Indeed it dislike fluorine so much that, apart from gaseous CuF, no other fluorine compounds of Cu(I) are known. Any attempts to form them results in the oxidation of Cu(I) to Cu(II). It is interesting, in passing, to compare this with Cu(II) where the soft iodide anion reacts with Cu(II) cations to form CuI and molecular iodine.

One of the consequences of the soft nature of Cu(I) is the fact that it readily forms bonds to carbon, forming compounds such as $(C_6H_5)_2Cu^-$ and the infinite polymer $(C_8H_8CuCl)_\infty$, while the reaction of metallic copper with gaseous acetylene to form the explosive cuprous acetylide resulted in a number of fatal accidents before it was realized that copper and all its alloys must be banished from the gas-cylinders used to store acetylene for welding.

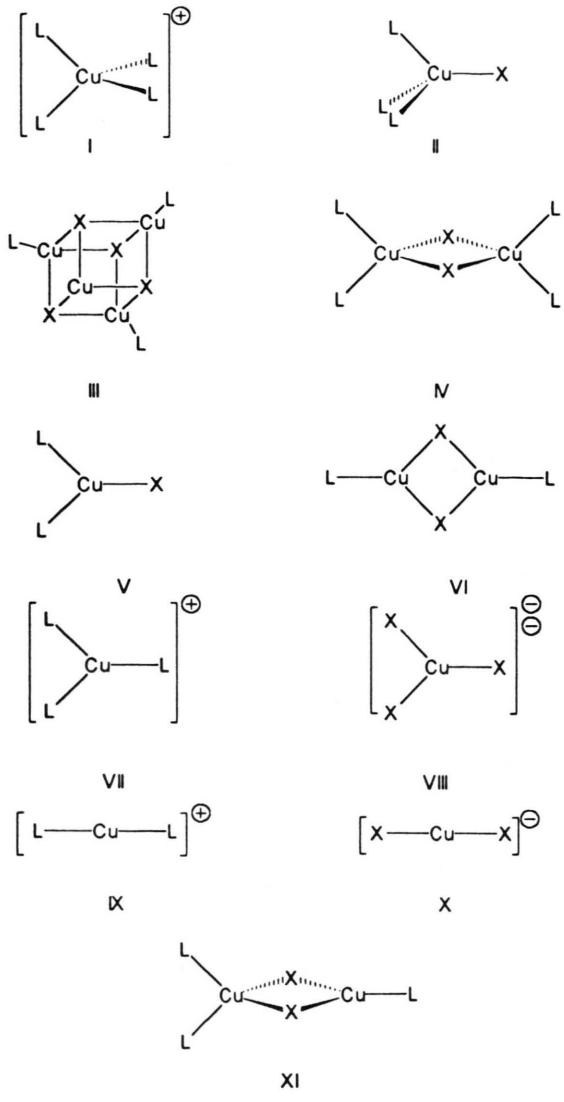
The complexes whose ^{63}Cu NQR spectra are reported here cover ligands whose donor atoms are nitrogen, phosphorus and sulphur together with the three halogens, chlorine, bromine and iodine, while the charge on the complexes ranges from positive through neutral to negative. We are only now undertaking the preparation and study of the more reactive complexes containing copper-carbon and copper-oxygen bonds.

Four-Coordinated Complexes

All other things being equal, the complexes of Cu(I) are four-coordinated with a tetrahedral configuration of the four ligands around the metal atom. Because of this preference for four-coordination the copper to ligand ratio of Cu(I) complexes is no guide to structure. Whenever possible the preferred tetrahedral configuration will be achieved by the formation of ligand, particularly halogen, bridges between several fragments, thus giving rise to polynuclear complexes. Examples of mononuclear and polynuclear four-coordinated structures are shown in **I**–**IV**.

Three-Corrdinated Complexes

The propensity to four-coordination can be overcome either if the ligands are too bulky for four ligands to be accommodated around the central atom or if the negative charge on the ligands is so great that the coulombic repulsion would destabilize the complex. Polynuclear complexes however can still be formed if the ligand to copper ratio is smaller than



two. Examples of such structures are shown in **V**–**VIII**.

Two-Coordinated Complexes

With very bulky or hard negatively-charged ligands such as Cl^- a linear two-coordinated structure becomes possible, **IX** and **X**. For border-line cases both two- and three-coordinated complexes of a given ligand can be prepared, e.g. **VII** and **IX.**

Mixed-Coordinated Complexes

Finally there exists a number of polynuclear complexes with copper atoms having both three- and four-coordination. An example is shown in **XI**.

Electronic Structure and Quadrupole Coupling Constants of ^{63}Cu Complexes

The neutral copper atom has the electronic configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9\,4s^2$ but the monovalent cation avoids the presence of two partially-filled shells by taking on the configuration $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$. Events take their normal course for the Cu(II) system which then has the $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$ electron configuration.

Table 2 shows the orbital energies of the neutral copper atom. The small differences between the energies of the outermost three orbitals are an indication of the ease with which the Cu(I) and Cu(II) systems may be expected to interconvert and of the highly-polarisable nature of the spherically symmetric Cu(I) cation.

Table 2. The Hartree-Fock orbital energies (in Hartrees) of the valence electrons of atomic copper.

3s	3p	3d	4s	4p
−5.26	−3.56	−0.74	−0.28	0

Table 3. The *m*-dependence of the one-electron field-gradients of p and d electrons in free atoms

$3d_z^2$	q_d
$3d_{xz}, 3d_{yz}$	$\frac{q_d}{2}$
$3d_{x^2-y^2}, 3d_{xy}$	$-q_d$
4s	0
$4p_z$	q_p
$4p_x\,4p_y$	$-\frac{q_p}{2}$

The Townes-Dailey Analysis of the Quadrupole Coupling in Copper Complexes

The usual Townes and Dailey analysis of quadrupole coupling constants relates them to the populations of the partially-filled p, d, f... orbitals. In the present system we need to consider the effects of both the 3d and the 4p electrons and, to this end, need to know how the different p or d orbitals of a given shell contribute to the field gradient (Table 3). The contributions of the 3d and 4p electrons are different and, for the isolated copper atom or cation, can be calculated from the Hartree-Fock radial wave functions [2]. The values thus calculated are shown in Table 4.

Table 4. The 3d and 4p one-electron coupling constants of ^{63}Cu. Theoretical values for free atomic or ionic ^{63}Cu in MHz. Taken from atomic SCF calculations and $Q = 220$ mb

	Neutral	Cu^+	Cu^{2+}	Cu^{3+}
3d	236	223	244	266
4p	49			

The Coupling Constants of Cu(II) Cations

Before discussing the results for Cu(I) presented above, it is appropriate to mention the results for Cu(II). The coupling constants of Cu(II) cations, the most usual oxidation state of the compounds of copper, have been measured for a wide variety of complexes through their Electron Spin Resonance spectra [3]. The complexes of Cu(II) are usually derived from a basic octahedral configuration of six ligands, usually with some degree of longitudinal deformation that, in the limit, leads almost to a square planar system. With hard ligands such as the sulphate anion, SO_4^{2-}, the Cu(II) cation is probably fairly close to the $3d^9$ configuration so that the coupling constant would be expected to be around 240 MHz, due to a positive hole in the $3d^{10}$ closed shell. The experimental values are 130–140 MHz, considerably smaller than this. With ligands that have a more marked covalent interaction with the Cu(II) cation the coupling constant falls drastically. This would be expected if the ligand electrons start to fill up the hole in the $3d^{10}$ shell, and also if they start to occupy the empty 4p orbitals and thus produce a field-gradient of opposite sign to that of the 3d hole.

The Bonding in CuX_2^-

The first serious attempts [4–6] to calculate the field gradients in Cu(I) complexes were due to Bowmaker et al. as recently as 1985. Using a variant of the Xα method they calculated the orbital populations in $CuCl_2^-$ shown in Table 5.

With the values of the atomic field-gradients given in Table 4 and the above populations for the atomic orbitals, the coupling constant in $[CuCl_2]^-$ is given by:

$$e^2 Q(0.210\,q_p - 0.051\,q_d) = 44.3\ \text{MHz}\,.$$

Since the atomic field-gradient for the 3d electron in the neutral Cu atom is five times that of the 4p

Orbital	Population
$3d_z^2$	1.829
$3d_{xz}$, $3d_{yz}$	2.051
$3d_{x^2-y^2}$, $3d_{xy}$	2.000
4s	0.795
$4p_z$	0.261
$4p_x$, $4p_y$	0.051

Table 5. The orbital populations in the $CuCl_2^-$.

Table 6. The *m*-dependence of the valence-electron coupling constants of ^{63}Cu in the $CuCl_2^-$ anion.

Orbital	Coupling constant per electron (MHz)
$3d_z^2$	214
$3d_{x^2-y^2}$, $3d_{xy}$	−229
$3d_{xz}$, $3d_{yz}$	114
$4p_z$	393
$4p_x$, $4p_y$	−231

Compound	3d	4p
CuF	220	349
CuCl	219	280
CuBr	220	257
CuI	220	238
$CuCl_2^-$	215	393
$CuBr_2^-$	216	365
Cu	236	49

Table 7. The one-electron 3d and 4p contributions (MHz) to the ^{63}Cu coupling constant in the cuprous halides and the cuprous dihalide anions.

Table 8. ^{63}Cu NQR frequencies of halocuprate Cu(I) anions.

Cation	Anion	ν_{77}	Ref.
[a] $[Bu_4N]^+$	$[CuCl_2]^-$	30.70	[8]
[b] $[Bu_4N]^+$	$[CuClBr]^-$	26.965	[9]
[a] $[Bu_4N]^+$	$[CuBr_2]^-$	28.85	[8]
[b] $[Et_4N]^+$	$[Cu_2Br_4]^{2-}$	30.647	[9]
[b] $[Bu_4N]^+$	$[Cu_2I_4]^{2-}$	24.385	[9]
[b] $[Me_4N]^+$	$[Cu_2Br_5]^{3-}$	31.397	[9]
[c] $[MePh_3P]^+$	$[Cu_2I_6]^{2-}$	26.15 26.80	[10]
[d] $[MePh_3P]^+$	$[CuI_3]^{2-}$	26.29 *	[11]

electron the field-gradient, the implication is that the coupling constant is dominated by the 3d term. The agreement between this theoretical value and the experimental one of 61.4 MHz is reasonably satisfactory, and the prospects for analyzing coupling constants in terms of a simple bonding picture thus are apparently favorable. Further investigation shows, unfortunately, that this is not the case.

In an isolated atom the radial functions of a given $l=1$(p) or $l=2$(d) sub-shell are all identical and independent of *m*, and the *m*-dependent field-gradient contributions are those given above. However the Cu(I) cation is highly-polarisable: this reveals itself in the value of the Sternheimer shielding parameter [7] which is much greater for $Cu(I)^+$ (−17.0) than for a non-polarisable "hard" cation such as Na^+ (−4.3). A consequence of this polarisability is that the radial functions of a given sub-shell vary with the orientation of the orbitals with respect to the molecular framework, and a marked *m*-dependence of the orbital field-gradient becomes apparent. The contributions of the individual 3d and 4p orbitals in $[CuCl_2]^-$ calculated by Bowmaker et al. [4] are shown in Table 6.

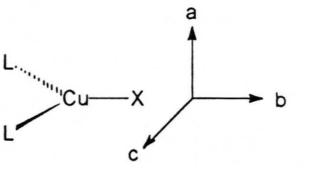
This shows that the $3d_z^2$ and the $3d_{x^2-y^2}$, $3d_{xy}$ orbitals have expanded, i.e. have a lower absolute value of the coupling constant, with respect to the $3d_{x^2-y^2}$, $3d_{xy}$ orbitals and to the 3d orbitals of the neutral Cu atom, while all three 4p orbitals have considerably contracted with respect to those of the free neutral copper atom, the contraction of the $4p_z$ orbitals, directed towards the neighboring halogen atoms being less marked than that of the $4p_x$, $4p_y$ orbitals. In this case the overall 3d orbital and 4p orbital contributions are of comparable magnitude, although the 4p contributions are now dominant:

$$3d = \quad 55 \text{ MHz}, \quad \text{Total} = 66 \text{ MHz},$$
$$4p = -121 \text{ MHz}, \quad \text{Exp. } 61.4 \text{ MHz}.$$

The agreement between theory and experiment is remarkably good but reveals the difficulty of analyzing the NQR data in terms of the orbital populations. There will usually be more "theoretical" parameters – orbital populations, one-electron coupling constants – than there are experimental parameters. Bowmaker et al. [4] have also performed calculations on diatomic copper compounds such as CuCl and found that here the 4p one-electron coupling constant is around 280 MHz while the $3d_z^2$ remains much the same as in $[CuCl_2]^-$. Finally, in both the one-coordinated and the two-coordinated systems, changing the halogen changes the 4p coupling constant in the sense Cl > Br > I while the 3d contribution remains fairly constant (Table 7). Although no calculations have been made for three-coordinate systems, we may reasonably anticipate that a similar behavior will prevail.

Table 9. Asymmetry parameters for three-coordinated complexes.

Complex	L	X	η	q_{xx}	q_{yy}	q_{zz}	Ref.
$(Ph_3P)_3Cu_2Cl_2$ [a]	Cl	Ph_3P	0.289	c	b	a	[12]
$(Ph_3P)_3Cu_2Br_2$ [a]	Br	Ph_3P	0.307	c	b	a	[12]
$(Ph_3P)_3Cu_2I_2$ [a]	I	Ph_3P	0.332	c	b	a	[12]
$(Ph_3P)_2CuBr$ [b]	Ph_3P	Br	0.113	b	c	a	[13]
(tetrahydropyrimidine-2-thione)$_2$CuCl [c]	$R_1R_2C=S$	Cl	0.362	c	b	a	[14]
$[NPr_4]_2Cu_2I_4$ [d]	I	I	0.262	b	c	a	[9]



In view of these facts it is clear that if we are to understand the coupling constants of Cu(I) complexes it will be necessary to have a sufficiently large body of data that will anable us to make use of our general chemical knowledge of the nature of the various components of these complexes in addition to the theoretical considerations just outlined. However, in so far as the 4p one-electron coupling constant is dominant, we may already anticipate that, for a given complex halide L_n CuX, the ^{63}Cu coupling constant will vary in the sense Cl > Br > I. This conclusion is born out by the data for a variety of polyhalocuprate anions (Table 8). By extension, for ligands other than halides we may expect that the coupling constant will increase as the electronegativity and hardness of the donor atom increases. In addition, if due consideration is taken of the effect of changes in molecular geometry, three-coordinated complexes are expected to have a greater coupling constant than their two-coordinated analogs. As we will see below, four-coordinated complexes have a tetrahedral geometry so that their coupling-constants should be small.

Survey of the ^{63}Cu Resonance Frequencies of Cu(I) Complexes

Introduction

If all four ligands are identical, as, for example, in the complex cation $(CH_3CN)_4Cu^+$, the field gradient at the copper atom is zero. If the ligands are different, then we may anticipate that the coupling constant will be small. "Small" is, however, a comparative term, and to put this in perspective this discussion concentrates on the Cu(I) coupling constants of the class of complexes that have been most extensively studied, namely three-coordinated complexes. The rather few values for four-coordinated species will be given in their appropriate context.

Three-Coordinated Complexes

In addition to the complexities introduced by the fact that, as will be seen below, there are two distinct valence-orbital contributions to the field-gradient tensor in Cu(I) complexes, the interpretation of the resonance frequencies of polycoordinated nuclei suffers from the difficulty of knowing how the field-gradient tensor is oriented with respect to the molecular framework. For trigonal planar systems such as $[CuI_3]^{2-}$ the direction of the field-gradient's z-axis is necessarily perpendicular to the molecular plane while the asymmetry parameter is zero. For systems where one of the ligands is different from the other two, A_2BCu, we may anticipate that the z-axis will remain perpendicular to the molecular plane provided that the difference between the ligands is not too great and that the angles ACuA and ACuB are not too different from 120°. In this case we may expect a regular change in resonance frequency as we explore changes in the structure of the three-coordinate complexes. On the other hand, if the electronic environment of the copper atom departs too much from the ideal three-fold symmetry the z-axis may change its direction and lie in the molecular plane. Should this occur, there will then be an unexpected change in the resonance frequency. This point will be addressed in more detail after the review of the data. However for the few compounds for which the orientation of the field-gradient tensor is available the z-axis always proves to lie perpendicular to the molecular plane (Table 9).

Phosphorus- and Sulphur-Containing Ligands

Apart from the very early detection of the resonances of Cu_2O and $KCu(CN)_2$ [15], the first extensive series of measurements of ^{63}Cu resonances dates from the 1970's when a number of complexes with sulphur- and phosphorus-containing ligands was investigated [16–22]. The majority of these were three-

Table 10. ^{63}Cu NQR frequencies of complex cuprous iodides with thione ligands, $[L_{3-n}CuI_n]^{1-n}$. The effect of charge.

Charge	Complex	ν_{77}	Ref.
+1	$[Cu(C_4H_6N_2S)_3Cu]^+[NO_3]^-$	32.549	[14]
0	$Cu(C_4H_8N_2S)_2CuI$	28.115	[14]
−1	$[Cu(C_4H_8N_2S)CuI_2]^-[(C_2H_5)_4N]^+$	27.996	[23]
−2	$[CuI_3]^{2-}([C_2H_5)_4N]^+)_2$	28*	[11]

* Estimated from the room-temperature frequency 26.29 MHz.

Table 11. ^{63}Cu NQR frequencies of complex cuprous bromides with phosphine ligands, $[L_{3-n}CuI_n]^{1-n}$. The effect of charge.

Charge	Complex	ν_{77}	Ref.
0	$(Ph_3P)_2CuBr$	33.93	[13]
−1	$[Ph_3PCuBr_2][(C_2H_5)_4N]$	33.197	[24]

Table 12. ^{63}Cu NQR frequencies of complex cuprous halides with thione ligands, $[LCuX_2]^-$ and L_2CuX. The effect of the halogen atom.

Complex	ν_{77}	Ref.
bis(N-methylimidazolidine-2-thione)CuCl	30.768	[25]
bis(N-methylimidazolidine-2-thione)CuBr	29.324	[25]
bis(N-methylimidazolidine-2-thione)CuI	28.150	[14]
[(N-ethylimidazolidine-2-thione)$CuCl_2$] [NEt_4]	33.001	[23]
[(N-ethylimidazolidine-2-thione)$CuBr_2$] [NEt_4]	30.417	[15]
[(N-methylimidazolidine-2-thione)CuI_2] [NEt_4]	27.996	[15]

Table 13. ^{63}Cu NQR frequencies of complex cuprous halides with phosphine ligands, $[LCuX_2]^-$ and L_2CuX. The effect of the halogen atom.

Complex	ν_{77}	Ref.
bis(Triphenylphosphine)CuCl	34.7*	[26]
bis(Triphenylphosphine)CuBr	33.93	[13]
[Triphenylphosphine $CuCl_2$] [NEt_4]	35.278	[24]
[Triphenylphosphine $CuBr_2$] [NEt_4]	33.197	[24]
[Triphenylphosphine CuI_2] [NPr_4]	29.710	[24]

* Extrapolated from the room-temperature frequency of MHz.

coordinated and, indeed, despite the impression conveyed by its formula, the $Cu(CN)_2^-$ anion is also a three-coordinated species. Our more recent observations have extended these studies to cover an entire range of mixed three-coordinated complex halides $[L_{3-n}CuX_n]^m$, where the charge, m, ranges from +1 for $n=0$ to −2 for $n=3$. A selection of results for three-coordinated mononculear complexes with either thione or phosphine ligands is shown in Tables 10–11. The most complete set of data, in Table 10, is available for thiones. As the charge on the copper atom becomes more positive the valence-orbitals would be expected to contract. The orbital field-gradients depend on $\langle r^{-3} \rangle$ and thus are expected to increase as the charge gets more positive. This effect, produced not by a change in formal charge but by the electron-withdrawing effect of an electronegative substituent, is the fundamental cause of the progression in one-electron orbital coupling constants in the series F > Cl > Br > I, that is illustrated for the diatomic cuprous halides in Table 7. It is thus not surprising that the coupling constant of the L_3Cu^+ cation is greater than that of the neutral L_2CuI. It is more surprising that further progressive replacement of thione ligands by I^- to form singly- and doubly-charged halocuprate anions does not result in any additional increase in resonance frequency. However, as we have already seen, the coupling constant arises from the difference between the contributions from the 3d hole and the 4p electron. Although Bowmaker's results for one- and two-coordinated compounds indicate that it is the 4p contribution that is most affected by the nature of the halogen atom, this may no longer be true for three-coordinated species. In any case, the one-electron contributions are weighted by the populations of the 3d and 4p orbitals so that an increase in the one-electron 4p field-gradient may be offset by a decrease in the 4p population, thus accounting for the observed constancy of the resonance frequency of the neutral and anionic species. However, as already mentioned, if the orientation of the field-gradient tensor with respect to the molecular framework is not the same in all these complexes, the association between the resonance frequency and the electronic structure of the complex is no longer straightforward.

The effect on the coupling constant of the nature of the halogen ligand, F > Cl > Br > I, in the series CuX and $[CuX_2]^-$ and the reasons for this effect have already been noted. Although, of course, no data for fluorine complexes are available, the results presented in Tables 12 and 13 show that the same trend is observed here, both for the neutral and negatively-charged species. A change of chlorine to bromine or from bromine to iodine results in a decrease of a little more than one megahertz per halogen atom. Thus in the anions, $L[CuX_2]^-$, two ligands are changed with every change of halogen, and the effect is about twice as big in these complexes as in the neutral ones.

Table 14. ^{63}Cu NQR frequencies of three-coordinated, L_2CuX, and four coordinated, $[L_2CuX]_2$ complex cuprous halides with pyridine ligands.

Complex	ν_{77}	Ref.
(2,6-lutidine)$_2$CuCl	38.350	[27]
(2,6-lutidine)$_2$CuBr	37.614	[27]
(2,6-lutidine)$_2$CuI	36.964	[27]
[(2-picoline)$_2$CuCl]$_2$	15.200	[28]
[(2-picoline)$_2$CuBr]$_2$	17.51	[28]
[(2-picoline)$_2$CuI]$_2$	14.787	[28]

Table 15. ^{63}Cu NQR frequencies of three-coordinate halogen-bridged complexes.

Complex	ν_{77}	Ref.
$[(C_6H_{11})_3PCuCl]_2$	31.473	[29]
$[(C_6H_{11})_3PCuI]_2$	29.408	[29]
$[(ortho\text{-}CH_3C_6H_4)_3PCuCl]_2$	32.592	[29]
$[(ortho\text{-}CH_3C_6H_4)_3PCuBr]_2$	30.884	[29]
[(2,6-lutidine)CuCl]$_\infty$	35.017	[30]
[(2,6-lutidine)CuBr]$_\infty$	32.055*	[30]
[(2,6-lutidine)CuI]$_2$	31.656 31.085	[27]

* Measured at room-temperature.

Table 16. ^{63}Cu NQR frequencies (MHz at room temperature) of mixed three- and four coordinated complex cuprous halides with triphenylphosphine ligands, $L_3Cu_2X_2$.

Complex	Three-coordinate	Four-coordinate	Ref.
$[(C_6H_5)_3P]_3Cu_2Cl_2$	29.95	13.47	[12, 26]
$[(C_6H_5)_3P]_3Cu_2Br_2$	28.36	14.31	[12, 26]
$[(C_6H_5)_3P]_3Cu_2I_2$	27.35	15.87	[12, 26]

Substituted Pyridine Ligands

In addition to the neutral three-coordinated phosphine and thione complexes, L_2CuX, we have also studied the analogous complexes where the ligand is a substituted pyridine molecule. In an extensive series of crystallographic investigations, A. H. White et al. have shown that the complexes, L_2CuX, formed by a heavily-hindered pyridine ligand such as 2,6-lutidine are three-coordinated whereas the apparently analogous complexes formed by a less hindered pyridine achieve four-coordination through the formation of a halogen-bridge. In confirmation of these results, Table 14 shows the ^{63}Cu NQR data for complexes of 2,6-lutidine and 2-picoline. On the one hand the resonance frequencies show clearly the change from three- to four-coordination in the complexes of 2-picoline, while on the other they show that the frequencies of the complexes of the hard nitrogen-based ligand are much greater than those of the softer phosphines and thiones. This effect is in complete accord with the trend already observed for the halide ligands.

Complexes with Halogen Bridges

Although quite a number of complex halides with a 1:1 ratio of L:Cu have been prepared, it usually turns out that the copper atom has increased its coordination number by the formation of halogen bridges. The resulting complex may either be an oligomer or an infinite polymer with either three-coordinated or four-coordinated copper atoms. In some cases the complex has both three- an four-coordinated centers. Those complexes that are uniquely three-coordinated are either dimers or infinite polymers (Table 15). Thus for the 1:1 complexes formed between 2,6-lutidine and the cuprous halides, the chloride and the bromide are infinite polymers while the iodide is a dimer. With phospines having bulky substituents attached to the phosphorus the complexes are dimers while for triphenylphosphine, in addition to the 2:1 monomeric complexes discussed above, mixed three- and four-coordinate halogen bridged complexes having the formula $L_3Cu_2X_2$ have been reported. The NQR method can be used to characterize complexes such as these owing to the considerable difference between the resonance frequencies of the three- and four-coordinated sites. Such an investigation was reported very early in the history of ^{63}Cu NQR by H. Negita et al. (Table 16).

It is interesting to compare the bridged halogen species with the corresponding $R_3PCuX_2^-$ anions, for in both cases the copper atom is surrounded by one ligand and two halogens. It is, perhaps, at first sight surprising that the anionic species have frequencies sligthly greater than those of the bridged dimers. The reason for this may lie in the considerable difference between the XCuX bond-angles for the anionic species (around 120°) and the bridged dimers (around 80°). This point is further discussed below.

Two- and Three-Coordinated Complex Cations with Pyridine Ligands

In addition to the complex halides discussed above, pyridine homologues with alkyl substituents in the

Complex	ν_{77}
(2,6-lutidine)$_2$BF$_4$	41.275
[(2,6-lutidine)$_2$Cu]PF$_6$	41.951
[(2,6-lutidine)$_2$Cu]ClO$_4$(β)	40.892
[(2,4,6-collidine)$_2$Cu]BF$_4$	41.170
[(2,4,6-collidine)$_2$Cu]CuCl$_2$	39.775

Table 17. ^{63}Cu NQR frequencies of two-coordinate Cu(I) cations with 2,6-lutidine or 2,4,6-collidine as ligand [31].

Anion	ν_{77}	Ref.
$[NO_3]^-$	32.650	[31]
$[CF_3CO_2]^-$	33.255	[31]
$[ClO_3]^-$	37.041	[31]
$[CF_3SO_3]^-$	39.220	[30]

Table 18. ^{63}Cu NQR frequencies of two-coordinate Cu(I) cations with 2,6-lutidine as ligand. The effect of partial bonding to the anion.

Table 19. ^{63}Cu NQR frequencies of two-coordinate Cu(I) cations with 2,6-lutidine or 2,4,6-collidine as ligand. The effect of Cu–N bond-length [33]

Complex	ν_{77}	Bond-length
[(2,6-lutidine)$_2$Cu]BF$_4$	41.275	1.904 (4)
[(2,6-lutidine)$_2$Cu]PF$_6$	41.951	1.898 (5)
[(2,6-lutidine)$_2$Cu]ClO$_4$(α)	39.400	1.936 (5)
[(2,6-lutidine)$_2$Cu]ClO$_4$(β)	40.892	1.912 (4)
[(2,6-lutidine)$_2$Cu]ClO$_4$(γ)	39.203	1.939 (3)
[(2,4,6-collidine)$_2$Cu]BF$_4$	41.170	1.900 (5)
[(2,4,6-collidine)$_2$Cu]CuCl$_2$	39.775	1.923 (3)

ortho position from two- and three-coordinated complex cations. Table 17 shows a selection of ^{63}Cu NQR frequencies for the heavily-hindered ligands 2,6-dimethylpyridine and 2,4,6-trimethylpyridine where the counter-anions are the hard, non-complexing species ClO_4^-, BF_4^- or PF_6^-. In these cations there is no uncertainty as to the direction of the field-gradient's z-axis. Structural studies have shown that all have linear N–Cu–N fragments and there can be no reasonable doubt that the z-axis lies along this. All have frequencies that are significantly but not considerably greater than the corresponding three-coordinate L_2CuCl complexes.

The crystal structure of the 2,6-lutidine complex with NO_3^- as the counter-ion suggested that in this case the oxygen atoms of the nitrate group also has a significant interaction with the metal atom, even though the N–Cu–N angle remains very close to 180°. The ^{63}Cu NQR frequency of this complex, 32.650 MHz, provides a striking confirmation of the difference between this complex and the preceding complexes with hard anions. Table 18 shows a selection of results with a variety of anions. Thus with the $CF_3CO_2^-$ anion the frequency is similar to that of the nitrate while with the trifluoromethylsulphonate anion, well-known to the organic chemist as a very hard species, has a frequency very similar to that of the perchlorates. The chlorate anion occupies an intermediate position.

In the course of our studies of the perchlorate of the *bis*(2,6-lutidine)Cu(I) cation it became apparent that this complex exhibits an interesting polymorphism. The first structure reported [32] for the complex showed that the dihedral angle between the two lutidine rings is zero so that all the atoms in the cation lie in the same plane. The complex that we had prepared turned out to have a structure where the dihedral angle between the lutidine rings is 58°, similar to the structures we had determined for the perfluoroborates of the *bis*(2,6-lutidine) and *bis*(2,4,6-collidine)-Cu(I) cations. The coplanarity of the ring systems results in steric hindrance between the methyl groups on the adjacent rings and an consequent lengthening of the Cu–Nu bond compared to that in the non-planar species, where the methyl groups avoid each other. These increases in bond-length reveal themselves clearly by a decrease of almost 2 MHz in the NQR frequency of the ^{63}Cu nucleus (Table 19).

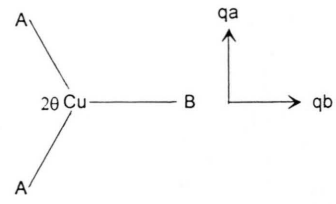
Although only one such complex had ever been previously reported, it turned out to be very simple to prepare three-coordinated cationic complexes of substituted pyridines. In almost all cases the frequencies are higher than those of the two-coordinated cations (Table 20), and almost by 50% greater than that of $[Cu(C_4H_6N_2S)_3Cu]^+ [NO_3]^-$ (Table 10), a representative of the only other type of three-coordinated cations to have been studied by ^{63}Cu NQR. Unlike the thione complexes, the pyridine complexes are non-planar with a propeller-like arrangement of the ligands around the metal atom. Of all the complexes reported in Table 20 the frequency of the complex (3,5-lutidine)$_3$PF$_6$ stands out as being significantly lower than the others. It is also remarkable in being the only complex that does not have substituents in the *ortho* position, and a structural study revealed that the absence of an *ortho* substituent permits the pyridine rings to adopt a paddle-wheel structure that, in turn, allows one of the fluorine atoms of the PF_6^- anion on each side of the complex to approach the copper atom. It is undoubtedly this weak interaction that is responsible for the marked decrease in the ^{63}Cu resonance frequency.

Table 20. ^{63}Cu NQR frequencies of three-coordinate Cu(I) cations with substituted pyridine ligands [33].

Complex	ν_{77}
[(2-picoline)$_3$Cu]PF_6	44.728
[2-ethylpyridine)$_3$Cu]ClO_4	45.450
[(2-benzylpyridine)$_3$Cu]PF_6	42.800
[(2,3-lutidine)$_3$Cu]PF_6	44.900
[(2,3-lutidine)$_3$Cu]PF_6	46.892
[(2,5-lutidine)$_3$Cu]PF_6	45.474
[(2,5-lutidine)$_3$Cu]PF_6	44.906
[(2,6-lutidine)$_3$Cu]PF_6	45.584
[(2,6-lutidine)$_3$Cu]PF_6	45.124
[(2,6-lutidine)$_3$Cu]PF_6	44.607
[(2,6-lutidine)$_3$Cu]ClO_4	44.554
[(2,6-lutidine)$_3$Cu]ClO_4	44.293
[(2,6-lutidine)$_3$Cu]BF_4	44.660
[(2,6-lutidine)$_3$Cu]BF_4	44.291
[(2,6-lutidine)$_3$Cu]BF_4	44.263
[(3,5-lutidine)$_3$Cu]PF_6	40.471
[(2-methyl, 5-ethylpyridine)$_3$Cu]PF_6	45.710
[(2-methyl, 5-ethylpyridine)$_3$Cu]ClO_4	43.219
[(2-methyl, 5-butylpyridine)$_3$Cu]PF_6	44.556
[(2,4,6-collidine)$_3$Cu]PF_6	44.832
[(2,4,6-collidine)$_3$Cu]PF_6	44.770
[(2,4,6-collidine)$_3$Cu]PF_6	44.592

The Effect of Bond-Angles on the ^{63}Cu NQR Frequencies

An inspection of the structural data for Cu(I) complexes reveals that for a given coordination number the bond-angles may show significant departures from the ideal values that would be observed if all the ligands were identical. Thus for planar three-coordinate complexes A_2CuB the ACuA angle may be markedly different from 120° while in a four-coordinated A_2CuB_2 the ACuA or BCuB angles may differ from the ideal tetrahedral angle. Without wishing to imply that the method is generally reliable for the interpretation of ^{63}Cu NQR data, it is instructive to make use of the partial-field gradient model to see what might be the possible effects of such changes on the coupling constants. In this method each ligand is supposed to contribute a cylindrically-symmetric partial field-gradient to the total field-gradient at the metal atom, this partial field-gradient being directed along the direction of the metal ligand bond. The resultant field-gradient may then be calculated from a knowledge of the molecular geometry and the partial field-gradients of each of the ligands. The results for the A_2BCu system afford a convenient example, particularly since the majority of the compounds for which the NQR data are available fall in this category.



If the partial field-gradients of A and B are represented by a and b, respectively, and the ACuA angle by 2θ then q_a and q_b, the components of the field-gradient tensor in the molecular plane perpendicular to and along the Cu–B bond, and q_c, the component perpendicular to the molecular plane are given by the equations:

$$q_a = 2a(3\sin^2\theta - 1) - b\,,$$
$$q_b = 2a(3\cos^2\theta - 1) + 2b\,,$$
$$q_c = -(2a + b)\,.$$

For three identical ligands and $\theta = 60°$ the asymmetry parameter is zero and the q_{zz} direction is q_c. For other combinations of the nature of the ligands the q_{zz} axis may lie along q_a, q_b, or q_c and, as the parameters are varied it may abruptly switch from one direction to another, as indeed will q_{xx} and q_{yy}. Despite this it can be shown that for a spin 3/2 nucleus such as ^{63}Cu, the resonance frequency is a smooth function of q_a, q_b, and q_c and thus of a, b, and θ:

$$\nu = e^2 Q \sqrt{q_a^2 + q_b^2 + q_c^2 - 2(q_a q_b + q_b q_c + q_c q_a)}\,,$$
$$\nu = e^2 Q \sqrt{12a^2\cos^4\theta - (12a^2 - 6ab)\cos^2\theta + 4a^2 - 2ab + b^2}\,.$$

The relationship between the asymmetry parameter and a, b, and θ depends on the correspondence between the directions of q_a, q_b, and q_c on the one and q_{xx}, q_{yy} and q_{zz} on the other. For most of the range of the parameters a, b, and θ, q_{zz} is perpendicular to the molecular plane. In that case the absolute value of η is given by:

$$|\eta| = \left| \frac{3}{2q_a + q_b}(1 + \cos 2\theta) \right|.$$

The sign of the function on the right hand side of the above equation is positive if q_{xx} lies along q_b and negative if it is q_{yy} that lies along q_b.

The following relationships are also useful in that they show where the q_{xx}, q_{yy} and q_{zz} directions of the

field-gradient tensor switch among the q_a, q_b, and q_c directions:

$$\eta = 0: \quad \cos 2\theta = -\frac{b}{2a},$$

$$|q_a| = |q_c|: \quad \cos\theta = \sqrt{\frac{a-b}{3a}},$$

$$|q_b| = |q_c|: \quad \sin\theta = \sqrt{\frac{2a+b}{6a}}.$$

It can furthermore be shown that the point at which the asymmetry parameter is equal to zero coincides with a minimum in the function relating the resonance frequency to the angle for a particular pair of partial field-gradients for the two ligands. The other two conditions indicate the positions where the asymmetry parameter becomes equal to one and the directions of the field-gradient principal values switch over.

The most interesting behavior of these equations occurs when the parameters of the two substituents are noticeably different. Figure 1 shows the angular dependence of the resonance frequency for three cases where the sum of the partial coupling constants is fixed at 60 MHz but where the relative values of the two partial-field gradients vary by a factor of the order of 2:1. In the neighbourhood of $\theta = 60°$ the slope of the frequency-angle relationship changes from positive when A has the largest partial coupling constant through zero when all three partial coupling constants are identical to negative when it is B that is the dominant partner. It should be stressed that it has not proved possible to characterize the ligands by unique values of their partial field-gradients that can be used to correlate the ^{63}Cu NQR data for a wide variety of complexes of different structural types. For this reason no undue weight should be attached to the actual numerical values that have been chosen for the corresponding partial coupling constants, $e^2 Q a$ and $e^2 Q b$; they have been chosen so that the resultant resonance frequencies fall in the range of those that we observe here. To illustrate these reservations, approximate values for the partial coupling constants of the phosphine, thione and halogens ligands for three-coordinated mononuclear complexes are given in Table 18. In Table 19 are shown a comparison of the experimental values of the resonance frequencies or, where available, the coupling constant and the asymmetry parameter, with the values calculated from the partial coupling constants of Table 18 and the known molecular geometry. It will be seen that the partial field-gradient model would appear to give a reasonably satisfactory account of the observed resonance frequencies of these complexes, and, for the two complexes for which the complete field-gradient tensor is known, yields not only an asymmetry parameter of the correct order of magnitude but also orients the three principal values correctly with respect to the molecular framework. The range of resonance frequencies covered by these complexes is however rather small, and the deficiencies of the method become at once apparent if an attempt is made to apply them to the complexes of 2,6-lutidine. A partial coupling constant of 30 MHz for this ligand may be at once obtained from the values for the three-coordinated cations shown in Table 17, and this value together with those already used for the halogens may be applied to the calcula-

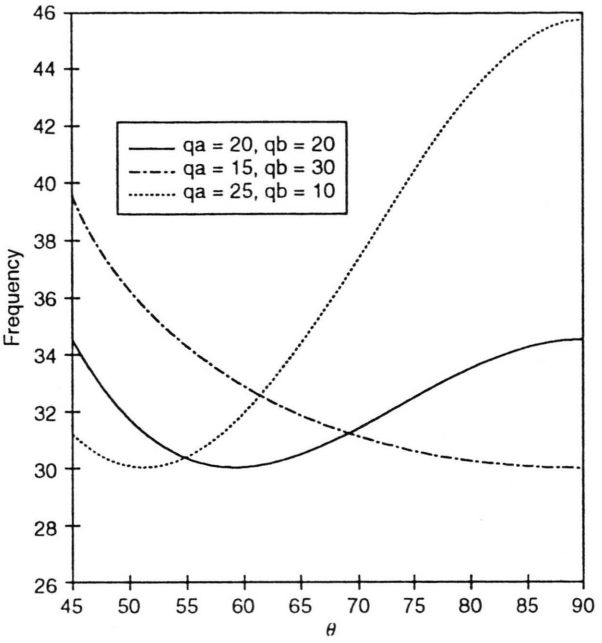


Fig. 1. Angular dependence of NQR for A2BCu complexes.

Ligand	$e^2 Q q_L$ (MHz)
Phosphine	22
Thione	21
Cl	23
Br	21
I	19

Table 21. Partial ^{63}Cu coupling constants for ligands in mononuclear three-coordinated complexes.

Complex	*a*	*b*	θ	Theory	Experiment
bis(triphenylphosphine)CuCl	22	23	63.0	33.6	34.700
bis(triphenylphosphine)CuBr	22	21	63.0	32.8	33.200
triphenylphosphine $CuCl_2$, Et_4N	23	22	58.1	34.0	35.278
triphenylphosphine $CuBr_2$, Pr_4N	21	22	59.9	32.0	33.197
triphenylphosphine CuI_2, Pr_4N	19	22	59.0	30.2	29.710
tris($C_4H_6N_2S$)$CuNO_3$	21	21	60.0	31.5	32.549
bis(tetrahydro-1-H-pyrimidine-2-thione)CuCl	21	23	59.1	32.6	30.200
N-ethylimidazolidine-2-thione CuI_2	19	21	61.3	29.5	27.996
bis(N-ethylimidazolidine-2-thione)CuCl	21	23	59.3	32.6	30.220
bis(N-ethylimidazolidine-2-thione)CuBr	21	21	58.1	31.6	29.393
bis(N-*n*-propylimidazolidine-2-thione)CuI	21	19	55.7	30.7	27.462
CuI_3^{2-}	19	19	60	28.5	28

Table 22. Comparison between experimental ^{63}Cu quadrupole coupling data and the values calculated from the partial ^{63}Cu coupling constants of Table 19 for mononuclear three-coordinated complexes.

Table 23 Comparison between experimental ^{63}Cu quadrupole coupling data and the values calculated from the partial ^{63}Cu coupling constants of Table 19 for mononculear three-coordinated complexes of 2,6-lutidine, partial coupling constant = 30 MHZ.

Complex	*a*	*b*	θ	Theory	Experiment
bis(2,6-lutidine)CuCl	30	23	69.8	45.9	38.350
bis(2,6-lutidine)CuBr	30	21	71.5	46.7	37.614
bis(2,6-lutidine)CuI	30	19	71.8	46.9	36.964

tion of the resonance frequencies of the monohalide complexes. The results are shown in Table 21; the agreement with the experimental values is completely unsatisfactory. Not only are the predicted values much higher than those observed but the relative frequencies of the three halides is not correctly predicted. However a detailed examination of the behavior of the three components of the field-gradient tensor predicted by the partial field-gradient model for such relatively large LCuL angles ($\approx 140°$) shows that the asymmetry parameter is close to unity and that, for the values of the partial field-gradients used, the *z*-axis switches from the direction perpendicular to the molecular plane to along the Cu–X bond as one goes from the chloride to the iodide. We have as yet no information as to the directions of the field-gradient tensors in these lutidine complexes.

Acknowledgements

All the results emanating from this laboratory are due to my collaborators, S. Ramaprabhu, A. Habiyakare, and N. Amstutz. Without the help of our crystallographer, G. Bernardinelli, it would have been impossible to interpret the results of our measurements with any degree of certitude. The Swiss National Research Fund is thanked for their support.

[1] B. J. Hathaway in Comprehensive Coordination Chemistry, Volume 5, Pergamon.
[2] C. Froese. J. Chem. Phys. **45,** 1417 (1966).
[3] L. W. White and R. L. Belford, J. Amer. Chem. Soc. **98,** 4428 (1975).
[4] G. A. Bowmaker, P. D. W. Boyd, and R. J. Sorrenson, J. Chem. Soc. Faraday Trans. 2 **81,** 1627 (1985).
[5] G. A. Bowmaker and P. W. Boyd, J. Mol. Structure (Theochem), **122,** 299 (1985).
[6] G. A. Bowmaker, Spectroscopy of Inorganic-based Materials, R. J. H. Clark and R. E. Hester, Eds., J. Wiley & Sons Ltd., New York 1987.
[7] P. W. Langhoff and R. P. Hurst, Phys. Rev. **139,** 1415 (1965).
[8] G. A. Bowmaker, L. D. Brockliss, C. D. Earp, and R. Whiting, Aust. J. Chem. **26,** 29 (1973).
[9] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. **1991,** 2615.
[10] G. A. Bowmaker, L. D. Brockliss, C. D. Earp, and R. Whiting, Aust. J. Chem. **26,** 2593 (1973).
[11] G. A. Bowmaker, G. R. Clark, D. A. Rogers, D. A. Camus, and N. Marisch, J. Chem. Soc. Dalton Trans. **1984,** 37.
[12] H. Negita, M. Hiura, K. Yamada, and T. Okuda, J. Mol. Struct. **58,** 205 (1980).
[13] T. Okuda, M. Hiura, and H. Negita, Bull. Chem. Soc. Japan **54,** 1920 (1981).
[14] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. **1993,** 1185.
[15] H. Krüger and U. Meyer-Berkhout, Z. Phys. **132,** 171 (1952).
[16] G. L. McKnown and J. D. Graybeal, J. Chem. Phys. **44,** 610 (1966).
[17] J. D. Graybeal and S. D. Ing, Inorganic Chem. **11,** 3104 (1972).
[18] H. Schmidbaur, J. Adlkofer, and K. Schwirten, Chem. Ber. **105,** 3382 (1972).
[19] G. A. Bowmaker, L. D. Brockliss, C. D. Earp, and R. Whiting, Aust. J. Chem. **26,** 29 (1973).
[20] T. J. Bastow and H. J. Whitfield, J. Inorg. nucl. Chem. **36,** 97 (1974).
[21] G. A. Bowmaker, R. Whiting, E. W. Ainscough, and A. M. Brodie, Aus. J. Chem. **28,** 1431 (1975).
[22] Y. Hiyama, N. Watanabe, and E. Niki, Bull. Chem. Soc. Japan **49,** 2986 (1976).
[23] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, to be published.
[24] S. Ramaprabhu and E. A. C. Lucken. Z. Naturforsch. **49a,** 193 (1994).
[25] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, Z. Naturforsch. **47a,** 125 (1992).
[26] T. Okuda, M. Hiura, K. Yamada, and H. Negita, Chemistry Letters, 367 (1977)
[27] A. Habiyakare and E. A. C. Lucken, J. Mol. Struct. **213,** 231 (1989).
[28] A. Habiyakare, E. A. C. Lucken, and G. Bernardinelli, Z. Naturforsch. **47a,** 106 (1992).
[29] S. Ramaprabhu, N. Amstutz, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. **1993,** 871.
[30] A. Habiyakare, Thesis, Université de Genève, (1990).
[31] A. Habiyakare and E. A. C. Lucken, Z. Naturforsch. **45a,** 224 (1990).
[32] L. M. Engelhardt, C. Pakawatchi, A. H. White, and P. C. Healy, J. Chem. Soc. Dalton Trans. **1985,** 117
[33] A. Habiyakare, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. **1991,** 2269.
[34] A. Habiyakare, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. **1992,** 2591.