^{63}Cu NMR Studies of Copper(I) Complexes in Solution: Influence of Anion, Solvent and Temperature on the Linewidth and Chemical Shift of the Copper Resonance

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The behaviour of the ^{63}Cu nuclear magnetic resonance signals in tetrahedrally coordinated copper(I) complexes has been investigated as a function of temperature, solvent and anion. From the strong dependence of the linewidth and the chemical shift on these parameters, exchange processes with complexes of lower symmetry are concluded.

Introduction

Over the past few years the application of NMR spectroscopy has been extended to a large number of heteronuclei, in addition to ^{13}C, ^{19}F or ^{31}P [1]. In the case of copper, however, relatively few investigations were performed in solution [2–9]. Hereby, the ^{63}Cu isotope was used predominantly, with a natural abundance of 69%, and a nuclear spin $I = 3/2$. Unfortunately, this nucleus has a rather large electric quadrupole moment, therefore reasonably narrow lines could only be observed in solution of copper (I) complexes with regular tetrahedral symmetry [6–9]. Systematic ^{63}Cu NMR investigations of the cuprous ion, tetrahedrally coordinated to phosphorus and nitrogen containing ligands, were performed in solution [6–9]. As a result from these experiments, the complex $Cu(P(OC_2H_5)_3)_4ClO_4$, dissolved in chloroform, was proposed as a convenient standard reference for ^{63}Cu NMR measurements [8], instead of the tetrakisacetonitrile complex, $Cu(CH_3CN)_4ClO_4$, used before. Clearly the NMR properties of this compound are very much dependent on temperature and the solvent, as recently reported [8, 9].

In this publication we wish to describe more detailed studies on a series of copper(I) complexes, CuL_4X ($L = CH_3CN$, or $P(OC_2H_5)_3$, $X = ClO_4^-$, BF_4^-, or p-$CH_3C_6H_4{-}SO_3^-$), with reference to the dependence of the chemical shift and linewidth on temperature, the nature of the counter anion, and the solvent.

Experimental

The ^{63}Cu NMR measurements were performed at approximately 23.86 MHz on a multinuclei Bruker pulse spectrometer SXP 4-100 in an externally stabilized magnetic field of 2.114 T. The free induction decays were accumulated and Fouriertransformed by the Bruker B-NC 12 data unit. The temperature of the sample was varied with a temperature control unit B-ST 100/700. Nonrotating cylindrical samples of 10 mm o.d. were used. The extremely constant magnetic field, which was stabilized by an external ^{1}H-NMR probe, allowed measurements of the ^{63}Cu Larmor frequency as a function of temperature without a second reference. The chemical shift was determined separately at room temperature (300 ± 1 K) by the sample exchange method, and reported as usual [6].

All copper(I) samples were prepared under the strict exclusion of dioxygen in an atmosphere of purified argon, using a Schlenk apparatus. The NMR tubes were carefully evacuated and refilled with argon at least five times, hereafter they were carefully sealed to protect the copper(I) compounds from air oxidation. All solvents were purified and dried by routine methods, as described in the literature [10]. The copper(I) complexes were synthesized according to the procedure of Hemmerich and Sigwart [11] and recrystallized from the appropriate

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solvent. EPR spectroscopy was applied to analyse for potential contaminations of the complexes by copper (II).

Results and Discussion

A) Influence of the Complex Anion and the Solvent

The chemical shift and linewidth data of the copper (I) acetonitrile cation with different counter anions in several solvents are collected in Table 1. Amongst the anions investigated are perchlorate, ClO_4^-, tetrafluoroborate, BF_4^-, and p-tosylate (p-Ts^-), p-$CH_3-C_6-H_4-SO_3^-$. Whereas both perchlorate and tetrafluoroborate gave relatively narrow NMR signals with linewidths of approx. 550 Hz, the corresponding tosylate exhibited much broader lines under identical conditions with a linewidth of 1200 Hz (Table 1, samples 1—3). In this context it should be mentioned, that in the solid tosylate complex only two acetonitrile ligands, instead of four, as in the perchlorate or the tetrafluoroborate, are bound to the copper (I) cation [11, 12]. The data in Table 1 clearly show, that in those samples, for which NMR signals of the copper (I) tetrakisacetonitrile complex could be detected, the chemical shift of the resonance line remains rather constant in different solvents, whereas the linewidth is remarkably dependent on the solvent applied. Surprisingly, no ^{63}Cu resonances could be detected for solutions of $Cu(CH_3CN)_4ClO_4$, 0.10 or 0.010 M in chloroform, methylene chloride or dimethylformamide.

Special attention must be attributed to the presence of water, as documented for the samples 4—9 in Table 1. Thus, an addition of small volumes of H_2O to the solution of the Cu (I) tetrakisacetonitrile cation in acetonitrile causes drastic line broadening of the ^{63}Cu resonance, i.e. 540 Hz vs. 900 Hz in 100% CH_3CN vs. 95/5% v/v CH_3CN/H_2O, a solvent with 95 volume per cent CH_3CN and 5 volume per cent H_2O. In 90/10% v/v CH_3CN/H_2O the line broadens further and becomes almost undetectable. In mixtures of water-acetonitrile containing strong acids, such as $HClO_4$, HBF_4, or p-toluene sulfonic acid (p-TsH), i.e. acids with poorly coordinating anions, the linewidth is slightly reduced again by comparison to the corresponding acid-free systems (Table 1, samples 7—9). This result is in close agreement with earlier investigations by Sigwart et al. [13] on the pH-dependent hydrolysis of $Cu(CH_3CN)_4^+$ in water-acetonitrile mixtures.

Generally, citation of linewidth values of ^{63}Cu resonances in solution should always be conscious of the problems discussed above, i.e. only extremely pure and carefully dried solvents should be employed. Another problem considered in this context are contaminations with paramagnetic copper (II). To test this for our NMR measurements, we added increasing amounts of aqueous copper (II) to a solution of $Cu(CH_3CN)_4BF_4$, 0.10 M in pure acetonitrile. Over a range of 99 μM through 476 μM Cu^{2+} added, i.e. under conditions with Cu (I)/Cu (II) = 1000 to 200, the linewidth of the ^{63}Cu line change

Table 1. Linewidths and chemical shifts of ^{63}Cu NMR signals in various tetrakisacetonitrile complexes. The chemical shifts are given relative to the new reference sample, a 0.1 molar solution of $Cu[P(OC_2H_5)_3]_4ClO_4$ in $CHCl_3$.

Nr.	Compound	Concentrat. of Cu (I) in molar	Solvent v/v in volume per cent	Linewidth $\Delta\nu$ in Hz	Chemical shift δ in ppm
1	$Cu(CH_3CN)_4ClO_4$	0.061	CH_3CN	550	-90 ± 2
2	$Cu(CH_3CN)_4BF_4$	0.087	CH_3CN	540	-91 ± 2
3	$Cu(CH_3CN)_2Ts$	0.11	CH_3CN	1200	-91 ± 3
4	$Cu(CH_3CN)_4ClO_4$	0.089	CH_3CN/H_2O, 91/9	2700	-101 ± 14
5	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 95/5	900	-91 ± 3
6	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 90/10	1215	-93 ± 3
7	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/0.10 M HBF_4-H_2O, 95/5	740	-92 ± 2
8	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/0.10 M HBF_4-H_2O, 50/50	2600	-107 ± 15
9	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/0.10 M HBF_4-H_2O, 10/90	— no signal	—
10	$Cu(CH_3CN)ClO_4$	0.062	CH_3CN/H_2O, 91/9; 180 μM Cu (II)	4800	-91 ± 19
11	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 99/1; 99 μM Cu (II)	560	-88 ± 3
12	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 98/2; 196 μM Cu (II)	620	-90 ± 3
13	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 95.25/4.75; 476 μM Cu (II)	850	-91 ± 4
14	$Cu(CH_3CN)_4BF_4$	0.10	CH_3CN/H_2O, 95.25/4.75; no Cu (II)	805	-91 ± 3

from 560 Hz to 850 Hz. By comparison, addition of equal amounts of Cu^{2+}-free water gave a maximum value of 805 Hz (Table 1, samples 10—14). This indicates, that the major contribution to line broadening indeed stems from water, and not from relaxation processes due to Cu(I)-Cu(II) electron exchange, as described earlier for the Cu(I)-Cu(II) chloride complexes [14].

In view of the large electric quadrupole moment of ^{63}Cu [6] we assume that the parameter most relevant for determining the linewidth is the coordination geometry around the copper center. Deviations from a perfect tetrahedral environment, as found for a large number of copper(I) complexes [2], will cause line broadening.

In pure acetonitrile the Cu(I) coordination sphere must be assumed to be tetrahedral for the tetrakisacetonitrile cation [14], in solvents such as chloroform, or methylene chloride, NMR silent species with trigonal or digonal symmetry, $Cu(CH_3CN)_2^+$ or $Cu(CH_3CN)_3^+$, and dimers of these complexes, will most likely be formed. In contrast, the tetracoordinated copper(I) complexes with phosphorus containing ligands are stable in these solvents because of the higher donor/acceptor strength of the ligands relative to acetonitrile [8]. If our conclusion is correct, that in acetonitrile, or other solvents described in Table 1, complexes of lower symmetry with coordination numbers of two and three can be formed, then all these complexes should be in rapidly exchanging equilibria. Consequently, we should observe a distinct temperature dependence of the linewidth of the ^{63}Cu resonance.

B) *Temperature Dependence of the Chemical Shift and Linewidth*

The temperature range covered in these experiments was approximately 100 K limited by the thermochemical properties of the solvents and copper(I) complexes. Figure 1 illustrates the Lamor frequency as a function of temperature for solutions of $Cu(CH_3CN)_4ClO_4$ in acetonitrile, and

$Cu[P(OC_2H_5)_3]_4ClO_4$

in chloroform. The temperature dependence varies significantly for the individual samples, particularly -0.75 ppm K^{-1} for the tetrakisacetonitrile complex, and approx. -0.1 ppm K^{-1} for the corresponding phosphorus complex. From these experimental results we deduce that the complex $Cu[P(OC_2H_5)]_4ClO_4$ should be a better standard reference [8]. This idea is further supported by data in Fig. 2, which represents the dependence of the linewidth on temperature. For all the samples investigated we find a decrease in linewidth with increasing temperature in the lower temperature region. This type of temperature dependence is expected for relaxation processes governed by quadrupolar relaxation mechanisms. Furthermore, an unexpected increase of the linewidth with rising temperature can be detected above approx. 280 K. Most certainly, this effect can be assigned to chemical equilibria exchange between tetrahedrally coordinated species and those with lower symmetry and coordination numbers. According to our discoveries, in the acetonitrile complexes the linewidth of the ^{63}Cu resonance is predominantly governed by these chemical exchange processes at temperatures higher than about 260 K. For the

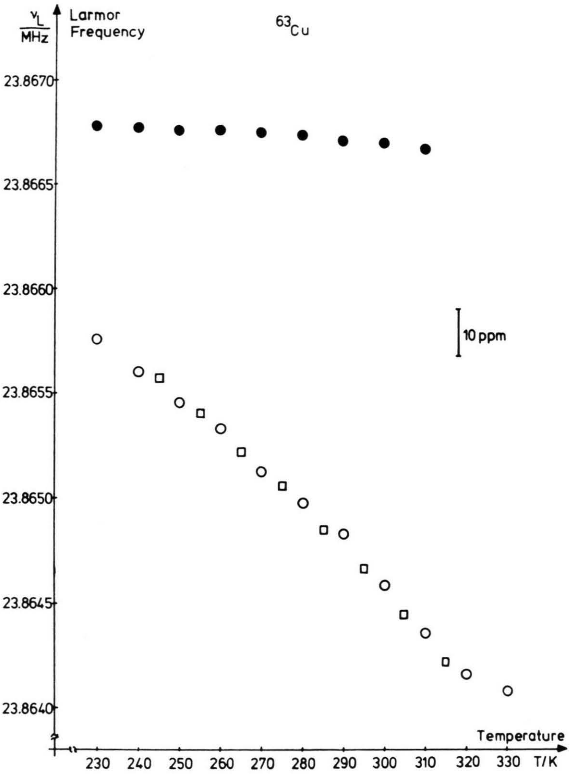

Fig. 1. Temperature dependence of the Larmor frequency of the ^{63}Cu NMR signal in some copper(I) complexes measured at 23.9 MHz:
● $Cu[P(OC_2H_5)_3]_4ClO_4$, 0.10 molar in $CHCl_3$;
○ $Cu(CH_3CN)_4ClO_4$, 0.061 molar in CH_3CN;
□ $Cu(CH_3CN)_4ClO_4$, 0.10 molar in CH_3CN.

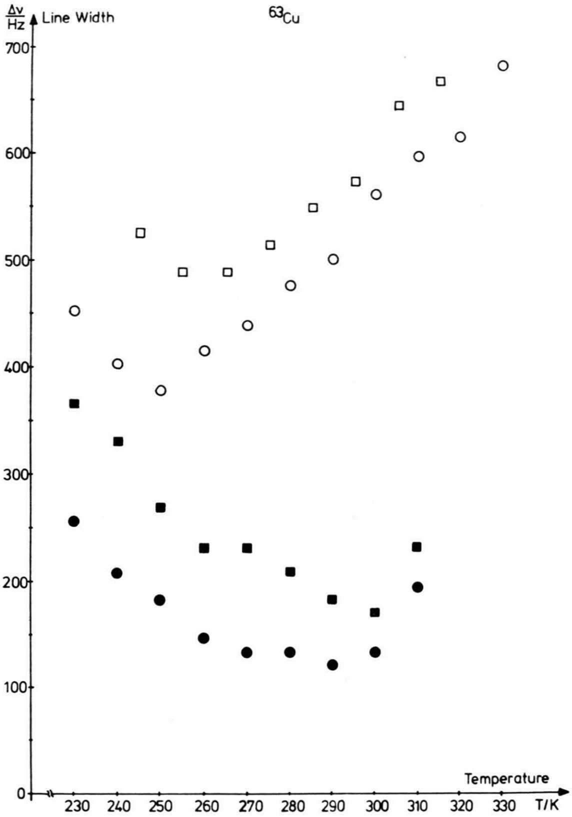

Fig. 2. Temperature dependence of the line width of the ^{63}Cu NMR signal in some copper(I) complexes measured at 23.9 MHz:
■ $Cu[P(OCH_3)_3]_4ClO_4$, 0.08 molar in $CDCl_3$;
● $Cu[P(OC_2H_5)_3]_4ClO_4$, 0.10 molar in $CHCl_3$;
○ $Cu(CH_3CN)_4ClO_4$, 0.061 molar in CH_3CN;
□ $Cu(CH_3CN)_4ClO_4$, 0.10 molar in CH_3CN.

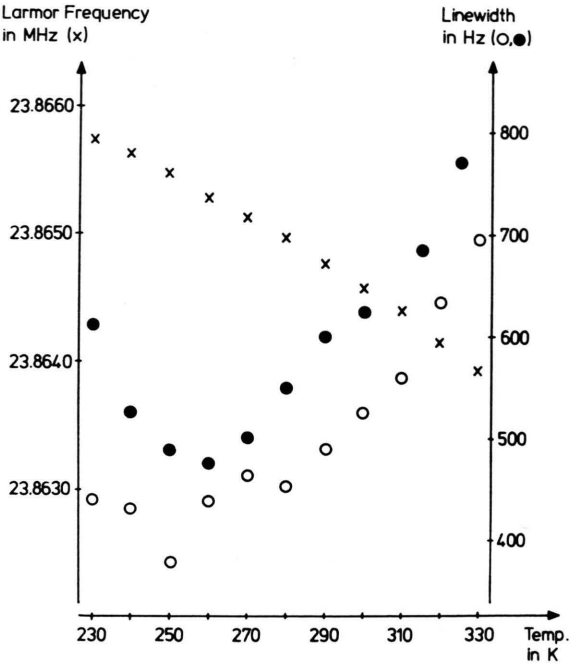

Fig. 3. Temperature dependence of the Larmor frequency and the linewidth of the ^{63}Cu NMR signals in acetonitrile complexes at 23.9 MHz:
○ $Cu(CH_3CN)_4BF_4$, 0.09 molar in CH_3CN;
●, × $Cu(CH_3CN)_4BF_4$, 0.10 molar in 99 vol% CH_3CN + 1 vol% H_2O.

copper(I) complexes with phosphorus ligands this specific increase in linewidth is measured at much higher temperatures, i.e. above about 300 K vs. about 200 K in the tetrakisacetonitrile complex. The temperature profiles shown in Figs. 1, 2, were observed independently of the concentration of the copper(I) complex, both in the case of the tetrakisacetonitrile and the phosphorus compound.

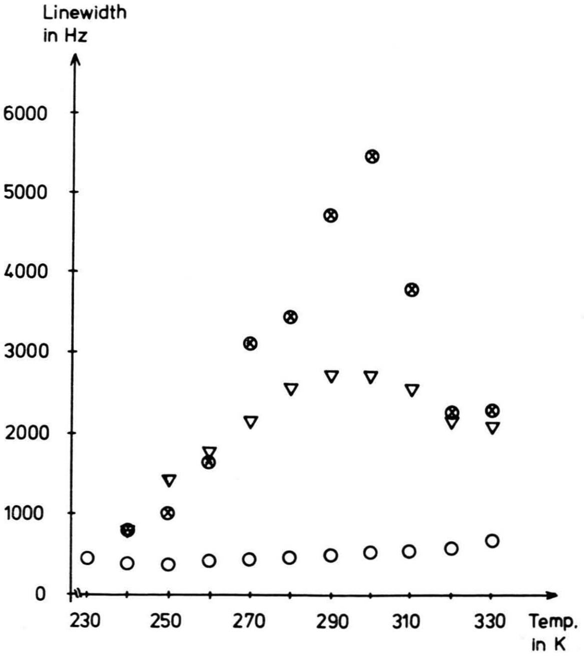

Fig. 4. Temperature dependence of the linewidth of the ^{63}Cu NMR signals in some acetonitrile copper complexes at 23.9 MHz:
○ $Cu(CH_3CN)_4ClO_4$, 0.061 molar in CH_3CN,
△ $Cu(CH_3CN)_4ClO_4$, 0.089 molar in 91 vol% CH_3CN + 9 vol% H_2O,
⊗ $Cu(CH_3CN)_4ClO_4$, 0.002 molar in 91 vol% CH_3CN + 9 vol% H_2O with 180 μ molar Cu(II).

Similar results were obtained for $Cu(CH_3CN)_4BF_4$ in acetonitrile as shown in Figure 3.

A completely different picture was observed for those samples containing water or water plus low concentrations of paramagnetic copper(II). As illustrated in Fig. 4 for the temperature dependence of the linewidth, maximum broadening of the ^{63}Cu resonance is detected for 290 K—300 K in samples containing approx. 9 vol% water. Both below and above this temperature the linewidth begins to decrease with drastic changes in the case of the sample, with Cu^{2+} added. On the other hand, the temperature dependence of the Lamor frequency exhibits the linear behaviour, observed for the water-free samples (Figure 1).

At present we can not give a reasonable and satisfactory interpretation for the temperature profile, found for those solutions of copper(I) complexes, containing water or both water and Cu^{2+}. In the system copper(I)-acetonitrile, addition of water will favor formation of Cu(I) complexes with only three or two CH_3CN ligands coordinated, as discussed at length in earlier publications on the solution chemistry of Cu(I) [12, 13]. This might explain the decrease in linewidth, with decreasing temperature in the presence of water, but the decrease above 300 K still remains obscure.

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