# $^{63}$Cu FT-NMR Studies of Tetrahedral Copper(I)-Phosphorus Complexes

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Tetrahedrally coordinated copper(I) complexes $CuL_4X$ have been synthesized, L being $P(OR)_3$, $PR_3$ or $P(R)_n(OR)_{3-n}$, and X being a non-coordinating anion such as perchlorate or tetrafluoroborate. Depending on the nature of the bound phosphorus ligand the Cu(I) complexes give well resolved $^{63}$Cu NMR spectra including a quintet signal due to spin-spin coupling between $^{63}$Cu and $^{31}$P. The $^{63}$Cu NMR spectra have been analyzed with reference to the chemical shift $\delta$, the shielding constant $\sigma^*$ (given on an absolute atomic scale), the linewidth $\Delta\nu$, and the coupling constant $J(^{63}$Cu-$^{31}$P). Generally, the relative magnitude of these NMR parameters are in satisfactory agreement with results reported for isoelectronic Ni(O) complexes with the phosphorus ligands mentioned above. Furthermore, the NMR properties of the Cu(I) compounds are discussed in terms of $\sigma$-donor or $\pi$-acceptor capacities of the ligands coordinated, and stereochemical properties of the complexes.

## Introduction

Over the past few years the technique of Nuclear Magnetic Resonance (NMR) was successfully applied to the investigation of numerous transition metal compounds, including those of biological interest, as reviewed in Ref. [1]. In the case of copper, which has two stable isotopes, $^{63}$Cu and $^{65}$Cu, both with a nuclear spin and magnetic moment, only a very limited number of NMR measurements were performed so far in the liquid state [2 – 7]. Hereby, tetrahedrally coordinated cuprous complexes such as $Cu(CH_3CN)_4ClO_4$ or the corresponding tetrafluoroborate compound were shown to be most suitable for NMR analysis yielding absolute shielding constants for both copper isotopes [6]. In addition, large chemical shifts, linewidths and spin-spin coupling constants $J(^{63}$Cu-$^{31}$P) could be determined for a series of different cuprous complexes [7]. These results clearly demonstrated that the NMR technique can develop into a rather powerful tool for the investigation of diamagnetic copper compounds. On the other hand, despite most favorable receptivities for both copper isotopes [6], no Cu NMR signal could be detected in several cuprous complexes of different coordination symmetries. This included also the photosynthetic electron-carrier plastocyanin (isolated from the alga *Scenedesmus* [8]), which in view of the symmetry at the copper site seemed to be rather suitable for Cu NMR [9].

In this paper we wish to report further systematic NMR measurements of tetracoordinated complexes of Cu(I) with phosphorus containing ligands. Investigations of this kind are necessary to enlarge the data basis of Cu NMR with reference to chemical shifts, linewidth and spin-spin coupling constants, which consequently will allow NMR experiments with more complicated systems as mentioned above.

## Experimental

The copper isotope $^{63}$Cu has a natural abundance of 69.1%, a nuclear spin $I = 3/2$ and a quadrupole moment $Q = -0.211 \cdot 10^{-28}\,\text{m}^2$ [10]. The Larmor frequency $\nu$ at 2.114 T is about 23.86 MHz. The NMR measurements were performed on a multinuclei Bruker pulse spectrometer SXP 4-100 at $(298 \pm 2)$ K in a magnetic field of 2.114 T externally stabilized by a Bruker NMR stabilizer B-SN 15. The free induction decays were accumulated and Fourier transformed by the Bruker B-NC 12 data unit. Non-rotating cylindrical samples of 10 mm o.d. were used. The chemical shifts are given in

$$\delta(\text{Cu}) = [\nu_{\text{sample}} - \nu_{\text{ref.}})/\nu_{\text{ref.}}].$$

A 0.1 molal solution of $Cu(CH_3CN)_4BF_4$ in dist. $CH_3CN$ was used as the reference throughout the

present investigation. Hereby the linewidth for $^{63}Cu$ was 540 Hz [6].

Detailed studies on the $^{63}Cu$ NMR properties of the cation $Cu(CH_3CN)_4^+$ with reference to different anions, concentration, solvent and temperature will be reported in a consecutive publication [11].

The shielding constant $\sigma^*$ of the reference is given on an absolute atomic shielding scale: $\sigma^*$ ($^{63}Cu$ in $Cu(CH_3CN)_4BF_4$, 0.1 molal in $CH_3CN$, vs. the free $Cu$ atom) $= -(1820 \pm 80) \cdot 10^{-6}$ (for details see [6]).

A typical $^{63}Cu$ NMR spectrum including all experimental parameters is shown in Figure 1. Due to our experience in copper NMR, $Cu[P(OC_2H_5)_3]_4ClO_4$ in chloroform is proposed as a more convenient reference sample.

All chemicals were commercially available in reagent grade. Acetonitrile and the phosphorus ligands were carefully purified by distillation or recrystallization from the appropriate solvent. The $Cu(I)$ complexes were prepared as described earlier [6, 7]. Hereby ETPB is used as abbreviation for 4-ethyl-2,6,7-trioxa-1-phospha-bicyclo-(2,2,2)-octane, and Tetraphos-2 for tris(2-diphenylphosphinoethyl)-phosphine. A detailed description of the synthetic procedure including the $^{31}P$ NMR data of the $Cu(I)$ compounds will be published elsewhere [12].

All NMR samples were handled under strict exclusion of dioxygen using purified argon as the inert gas. In most cases the NMR tubes were sealed under argon to allow careful studies over a longer time period.

## Results and Discussion

### 1. Classification and properties of tetracoordinated complexes $CuL_4X$, X being a non-coordinating anion

The phosphorus ligands used in this work are devided into three categories (Table 1):

a) Phosphites $P(OR)_3$, R being an aliphatic or aromatic residue.

b) Phosphines $PR_3$, R as in a).

c) "Mixed" phosphines $P(R)_n(OR)_{3-n}$, R as in a) or b).

Cuprous complexes with the ligands mentioned above have been investigated in great detail, applying $^{31}P$ NMR [13], X-ray diffraction [14, 15] conductivity measurements [16] or other techniques [17]. Although in many cases no crystal structure is available at present, tetrahedral or pseudotetrahedral geometry is assumed for $CuL_4X$ both in solution and in the crystalline state. Furthermore, $CuL_4X$ is regarded to be the dominant species in solution [13 – 17], although in cases of R being an aromatic residue several mononuclear and polynuclear complexes can exists, i.e. $CuL_3X$, $CuL_2X$ or $Cu_2L_3X_2$ depending on the coordinative properties of X [17]. On the basis of elementary analysis all the $Cu(I)$ complexes listed in Table 1 have a metal to phosphorus ratio of 1 : 4. This is also true for the rather constrained ligand ETPB, 4-ethyl-2,6,7-trioxa-1-phospha-bicyclo-(2,2,2,)-octane, as demonstrated by the well resolved $^{31}P$ [12] and $^{63}Cu$ NMR spectra. In contrast hereto, triscyclohexylphosphine [16] will only form the 2 : 1-complex $CuL_2X$, X being a halogenide or nitrate anion [17, 18], due to steric overcrowding at the $Cu(I)$ nucleus. Consequently, no $^{63}Cu$ NMR signals have been detected for the products of the reaction of $Cu(CH_3CN)_4ClO_4$ with $P(C_6H_5)_3$ and $P(C_6H_{11})_3$ in agreement with the results reported earlier [7].

### 2. $^{63}Cu$ NMR properties of tetracoordinated complexes $CuL_4X$

Table 1 summarizes the NMR parameters of the copper complexes investigated in this work, with



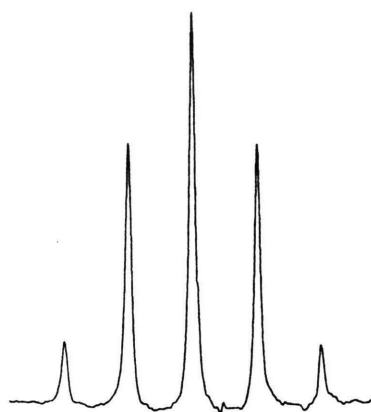Fig. 1. $^{63}Cu$ FT NMR signal near 23.860 MHz of a 0.1 molar solution of $Cu(I)[P(OC_2H_5)_3]_4ClO_4$ in $CHCl_3$ with a linewidth of 137 Hz. Experimental spectrum width: $2 \times 25$ kHz (quadrature), number of pulses: 1600, measuring time: 8 min, $2 \times 600$ data points were accumulated, followed by $2 \times 7592$ points of zerofilling before Fourier transformation.

Table 1. $^{63}$Cu NMR parameter of tetracoordinated Cu(I) complexes with phosphites (compounds 1—7), phosphines (compounds (8—10) and "mixed alkoxyphosphines" (compounds 11—15). Each sample contains approx. 0.8 g/1.8 ml chloroform giving a 0.1 M solution. Sample No. 1 is dissolved in $CDCl_3$.

| No. | Compound $CuL_4ClO_4$ | Chemical shift $\delta$ (ppm) | Shielding constant $\sigma^*/10^6$ | Line width $\Delta\nu$/Hz | Coupling constant $J(^{63}Cu\text{-}^{31}P)$/Hz |
|---|---|---|---|---|---|
| 1 | $Cu[P(OCH_3)_3]ClO_4$ | 82(1) | − 1902 | 166 | 1223(10) |
| 2 | $Cu[P(OC_2H_5)_3]_4ClO_4$ | 88(1) | − 1908 | 137 | 1209(8) |
| 3 | $Cu[P(OCH(CH_3)_2)_3]_4ClO_4$ | — | — | — | — |
| 4 | $Cu[P(OC_4H_9)_3]_4ClO_4$ | 91(1) | − 1911 | 430 | 1312(20) |
| 5 | $Cu[ETPB]_4ClO_4$ | 73(3) | − 1893 | 750 | 1458(70) |
| 6 | $Cu[P(OC_6H_5)_3]_4ClO_4$ | — | — | — | — |
| 7 | $Cu[P(O\text{-}p\text{-}Cl\text{-}C_6H_4)_3]_4ClO_4$ | — | — | — | — |
| 8 | $Cu[P(CH_3)(C_6H_5)_2]_4ClO_4$ | — | — | — | — |
| 9 | $Cu[Tetraphos\text{-}2]ClO_4$ | — | — | — | — |
| 10 | $Cu[P(CH_3)_2(C_6H_5)]_4ClO_4$ | 247(4) | − 2067 | 2750 | — |
| 11 | $Cu[P(OCH_3)(C_6H_5)_2]_4ClO_4$ | 178(5) | − 1998 | 4250 | — |
| 12 | $Cu[P(OCH_3)_2(C_6H_5)]_4ClO_4$ | 136(1) | − 1956 | 530 | 1109(33) |
| 13 | $Cu[P(OC_2H_5)_2(C_6H_5)]_4ClO_4$ | 138(1) | − 1958 | 520 | 1113(40) |
| 14 | $Cu[P(OC_4H_9)(C_6H_5)_2]_4ClO_4$ | 173(5) | − 1993 | 4130 | — |
| 15 | $Cu[P(OC_4H_9)_2(C_6H_5)]_4ClO_4$ | 134(1) | − 1954 | 650 | 1200(70) |

reference to the chemical shift $\delta$, the shielding constant $\sigma^*$, the linewidth $\Delta\nu$, and the coupling constant $J(^{63}Cu\text{-}^{31}P)$.

a) **Chemical shift and shielding constant**: With respect to $\delta$ of the $^{63}$Cu NMR signal clearly the phosphite complexes (Table 1, compounds 1 – 7) exhibit the smallest values ranging from 73 ppm for the ETPB complex to 91 ppm in the case of the tributylphosphite complex. The chemical shift is drastically increased upon coordination of a phosphine to Cu(I), as demonstrated for the Cu(I) complex of dimethylphenylphosphine (compound 10), which now gives a $\delta$-value of 247 ppm. Intermediate values of the chemical shift are obtained for the "mixed" phosphorus ligands $P(R)_n(OR)_{3-n}$, such as $P(C_6H_5)(OCH_3)_2$. Its Cu(I) complex (compound 12) gives a $\delta$ of 136 ppm vs. 88 ppm in $Cu[P(OCH_3)_3]_4ClO_4$ (compound 1) or 178 ppm in $Cu[POCH_3(C_6H_5)_2]_4ClO_4$ (compound 11). Within the series of phosphite complexes the differences in $\delta$ are relatively small compared to the differences discussed above. The lowest $\delta$ value, 73 ppm, is measured for the ETPB complex which is 15 ppm lower than the corresponding Cu(I) complex of trimethoxyphosphite.

With reference to $\delta$, comparable results have been obtained by Tolman [19, 20] for a series of zerovalent Ni complexes with the phosphorus ligands of

Table 1. From his data it can be readily seen, that there is no general correlation between 1) the $^{31}$P chemical shift of the free ligand, and 2) with the $^{31}$P chemical shift of the Ni(O) complex with the electron donor or $\pi$-acceptor character of the coordinated ligand. Thus, despite a large electronic difference between $P(OC_2H_5)_3$ and ETPB on the basis of IR studies, yet the stabilities of the corresponding tetrakis Ni(O) complexes are the same. Furthermore, despite $P(OC_6H_5)_3$ being a much stronger $\pi$-acceptor for metal $\xrightarrow{\pi}$ ligand back donation in comparison to $P(OC_2H_5)_3$, the ethyl derivative forms the stronger complex with Ni(O). The dominant factor governing the stability of the Ni(O) complexes seems to be linked to stereochemical properties of the ligand, i.e. the so-called cone angle occupied by the bound ligand at the metal nucleus. Thus, in the series of $P(OR)_3$ ligands the cone angle increases from ETPB, $CH_3$, $C_2H_5$, $C_4H_9$, $CH(CH_3)_2$, $C_6H_5$. For ETPB a value of $(106 \pm 2)°$ has been calculated vs. $(145 \pm 2)°$ in the case of $P(OC_6H_5)_3$. Much larger angles are derived for the analogous phosphine complexes, i.e. $(118 \pm 4)°$ for the $P(CH_3)_3$ complex vs. $(145 \pm 2)°$ in the $P(C_6H_5)_3$ complex or $(179 \pm 10)°$ in the $P(C_6H_{11})_3$ species.

b) **Linewidth**: As already pointed out in an earlier communication within this series [7], reasonably narrow lines are only observed for those

cuprous complexes having a tetrahedral coordination symmetry, i.e. a symmetric charge distribution at the copper nucleus. Thus, digonal and trigonal planar copper complexes were practically NMR silent, as described in Ref. [6] and [7]. A second factor influencing the linewidth of the $^{63}$Cu NMR signal seems to be linked to the metal $\pi$ ligand acceptor properties of the phosphorous ligand, as documented for the increasing linewidth within the series $CH_3CN <$ pyridine $<$ bipyridine or o-phenanthroline. These earlier findings are supported by the data collected in Table 1, column 3. Thus, by substituting an aromatic residue R for an aliphatic R the linewidth of the copper NMR signal generally increases, as documented by the series of complexes $Cu[(R^1)_n(OR^2)_{3-n}P]_4X$ with $R^1$ being $C_6H_5-$ and $R^2$ being $CH_3-$ (compounds 1, 11 and 12). The NMR silence of the triphenylphosphite complex (compound 6) or its p-chlor-derivative (compound 7) could be due to the same effect, also in these two cases $CuL_4X$ might not be the dominant species in solution, as most likely in the case of the tris-i-propylphosphite complex (compound 3), due to steric hindrance, in agreement with other investigations [17, 18, 20]. In this context it should be noted that in the corresponding $^{31}$P NMR spectra (measured at 298 K) of these $^{63}$Cu NMR silent complexes a relatively broad line is observed with no fine structure resulting from Cu-P spin-spin-interaction [12]. On the other hand, for the majority of the copper complexes summarized in Table 1 which show a $^{63}$Cu NMR signal, well resolved quartets were found for the $^{31}$P resonance in chloroform solution. As mentioned earlier by Tolman [20], substitution of alphatic groups by phenyl groups at the phosphorus increases the cone-angle of the ligands coordinated to copper drastically. This increase is paralleled by increase of the ligand exchange rate.

c) **C o p p e r - 6 3 - P h o s p h o r u s - 3 1  S p i n - S p i n  C o u p l i n g** $J(^{63}$Cu-$^{31}$P): From the values for $J(^{63}$Cu-$^{31}$P) listed in Table 1 it can be deduced, that $J$ is always larger for the phosphite complexes than for the phosphine complexes. Typically, the cuprous ETPB compound exhibits the largest coupling constant of 1458 Hz amongst the complexes investigated, whereas for comparison

$$Cu(I)[P(OCH_3)_2(C_6H_5)]ClO_4$$
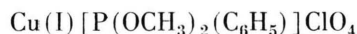
gives a value of approx. 1110 Hz. This result agrees very well with earlier experiments on tungsten complexes with phosphorus ligands by Keiter and Verkade [21]. These authors explain the increase of $J(^{183}$W-$^{31}$P) with increasing electronegativity of the bound phosphorus, i.e. increase of the $\sigma$-character of the metal-phosphorus bond, or increase of the positive charge on the liganded phosphorus atom. Within the series of phosphite compounds the following upward trend for $J(^{63}$Cu-$^{31}$P) is found:

$$P(OCH_3)_3 \approx P(OC_2H_5)_3 < P(OC_4H_9)_3 < ETPB.$$
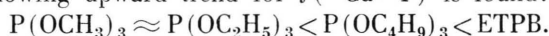
Again, this trend was also found for the corresponding tungsten complexes [21], and correlated to the decreasing $\sigma$-donating capacity of the coordinated phosphorus atom. Other factors influencing the magnitude of $J$, such as the cone angle [20], the ionization potential of the metal, or the partial charge on the phosphorus nucleus and its polarizability must be considered as discussed at length in [13].

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