Chemical Shifts and Coupling Constants in Copper (I)-Compounds by ^{63}Cu and ^{65}Cu FT-NMR Studies

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Using ^{63}Cu and ^{65}Cu FT NMR, chemical shifts and large indirect spin-spin-coupling constants with phosphorus were measured in dissolved copper(I) compounds. The nuclear magnetic shielding constants derived from the chemical shifts were given in the atomic reference scale. No isotope effect for spin-spin-coupling constants was found.

Introduction

In recent years the technique of Nuclear Magnetic Resonance (NMR) has been successfully applied to heavier metals such as molybdenum [1], manganese [2] or vanadium [3]. Although this method is restricted to diamagnetic compounds, sufficient structural information can be obtained as demonstrated for the series of thiomolybdates $MoO_{4-n}S_n^{2-}$ $(n = 0-4)$ (Ref. [1, 4]). This is especially true for those nuclei with small nuclear quadrupole moments which do exhibit narrow resonance lines.

In the case of copper two isotopes, ^{63}Cu and ^{65}Cu with both a nuclear spin $I = 3/2$, are susceptible to NMR. Due to their large natural abundance of 69.1% and 30.9% and the rather large magnetic moment [5] the receptivities are satisfactory. Despite these favourable nuclear properties only few copper NMR studies have been performed in solution so far [6–9]. This mainly because of the presence of strong quadrupole interaction in both isotopes causes line broadening in those cuprous complexes with a residual field gradient at the copper nucleus.

In a recent paper on FT NMR studies of several cuprous compounds it is shown, that the nuclear magnetic shielding of copper can be given in an atomic reference scale [10, 11]. In this communication we wish to report further measurements of chemical shifts in cuprous complexes including the observation of indirect spin-spin-coupling to coordinated ^{31}P nuclei.

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Experimental

All measurements were performed on a multinuclei Bruker pulse spectrometer SXP 4-100 in a magnetic field of 2.114 T, externally stabilized by the Bruker NMR stabilizer B-SN 15. The free induction decays were accumulated and Fourier transformed by the Bruker B-NC 12 computer. Nonrotating cylindrical samples of 10 mm outer diameter were used. The temperature was (298 ± 2) K. According to the rules for presenting NMR data of heteronuclei [12] the chemical shifts are given as

$$\delta(\mathrm{Cu}) = [(\nu_{\mathrm{sample}} - \nu_{\mathrm{ref.}})/\nu_{\mathrm{ref.}}] \cdot 10^{+6}.$$

The reference sample was a 0.1 molal solution of $Cu(I)(CH_3CN)_4BF_4$ in CH_3CN, the linewidth for ^{63}Cu was 540 Hz.

All cuprous compounds were handled under strict exclusion of oxygen in an atmosphere of purified argon or nitrogen. $Cu(CH_3CN)_4ClO_4$ was prepared according to the method of Sigwart and Hemmerich [13]. The corresponding tetrakis (pyridine) Cu(I) complex was obtained by dissolving a proper amount of the acetonitrile complex in dry pyridine and evaporation to dryness. Similarly $Cu[P(OR)_3]_4ClO_4$ with $R = -CH_3$ and $-C_2H_5$ was prepared by adding 2 g of the acetonitrile complex to 50 ml of the corresponding phosphite. The resulting suspension was refluxed for 60 minutes, upon cooling to room temperature 3–4 g of white crystals could be isolated by filtration. The solid white material was recrystallized from CH_2Cl_2/ether. The purity of all cuprous complexes synthesized was checked by elementary analysis.

Results and Discussion

A) Chemical Shifts

The results of chemical shift measurements are presented in Table 1. Whereas in the case of molybdenum thiomolybdates large chemical shifts from up to 2000 ppm have been observed upon exchange of oxygen against sulfur ligands [1], no such tremendous differences could be obtained for the cuprous complexes investigated in this paper. Furthermore no significant dependence on the concentration of the cuprous complex has been found (Table 1). Figure 1 illustrates the chemical shifts measured and expressed in terms of an atomic shielding scale [10, 11] including extra data from the literature [7, 8]. On this scale chemical shifts are referred to the free copper atom, which is much more meaningful than those basing on arbitrary reference compounds.

In all complexes of this series cuprous copper is coordinated to four nitrogen or phosphorus ligands capable of metal to ligand back donation [14]. Among the ligands pyridine nitrogen seems most suitable for lowering the electron density at the cuprous site. Surprisingly no copper NMR signals could be detected in a reasonable time interval for the corresponding cuprous complexes of bipyridine, o-phenanthroline and derivatives. This is also true for the sulfur-containing ligands such as methionine and 1,2-bis(carboxymethylmercapto)ethane, which are known to form well defined tetrahedral complexes both in solution and the crystalline state [15]. Although at present only few data are available on copper NMR, the experimental results described above suggest, that the lack of a copper resonance line originates from strong quadrupole interaction

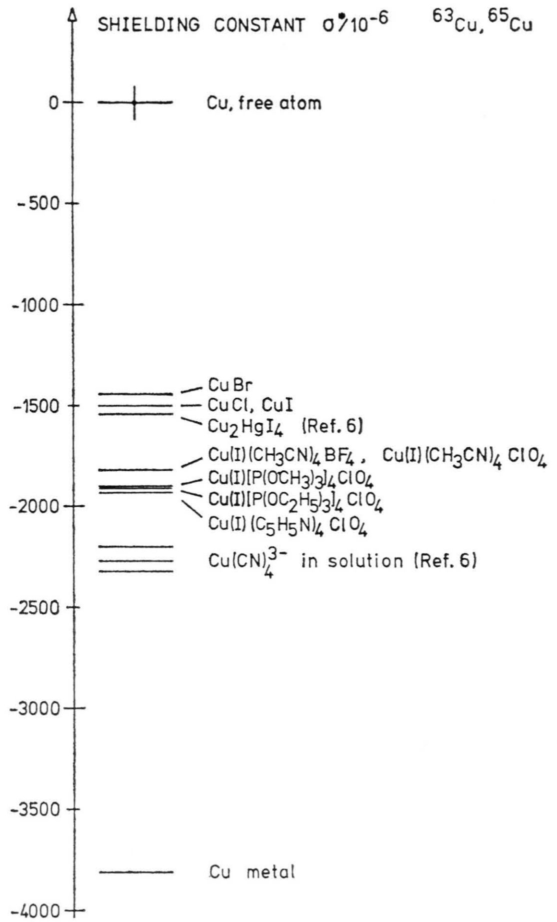

Fig. 1. Atomic reference scale of the nuclear magnetic shielding of copper. The shielding constant σ^* of the refe-rence compound of the present work is:

$$\sigma^* = -(1820 \pm 80) \cdot 10^{-6} \text{ (Ref. [11])}$$

the error results from the atomic beam measurement [10] as indicated. For cyanide solutions and Cu_2HgI_4 data of Ref. [8] and for solid samples data of Ref. [11] were used.

Table 1. Chemical shifts and linewidths of some copper (I) compounds at different concentrations. The reference sample is a 0.1 molal solution of $Cu(I)(CH_3CN)_4BF_4$ in CH_3CN. The linewidth for the samples 6–8 is that of the central line of the multiplet observed.

Sample	Solvent	Concentration (Molal)	Chemical Shift δ	Typical Linewidths in Hz
1 $Cu(I)(CH_3CN)_4ClO_4$	CH_3CN	0.1	0.1 ± 0.5	650
2 $Cu(I)(CH_3CN)_4ClO_4$	CH_3CN	0.01	-0.9 ± 0.9	500
3 $Cu(I)(CH_3CN)_4ClO_4$	CH_3CN	0.005	-0.3 ± 1.4	500
4 $Cu(I)(C_5H_5N)_4ClO_4$	C_5H_5N	0.1	110 ± 2	1450
5 $Cu(I)(C_5H_5N)_4ClO_4$	C_5H_5N	0.05	111.1 ± 1.4	880
6 $Cu(I)[P(OCH_3)_3]_4ClO_4$	$P(OCH_3)_3$	0.08	82.6 ± 0.5	115
7 $Cu(I)[P(OCH_3)_3]_4ClO_4$	$P(OCH_3)_3$	0.04	82.6 ± 0.2	115
8 $Cu(I)[P(OC_2H_5)_3]_4ClO_4$	$P(OC_2H_5)_3$	0.1	91.8 ± 0.4	310

due to a residual electric field gradient at the copper nucleus. Two reasons might be responsible for this asymmetric charge distribution. In the first place a slight distortion from regular tetrahedral geometry could occur, and second, strong metal to ligand back donation might influence the charge distribution. Thus from the cuprous compounds compiled in Table 1 the tetrakis (pyridine) Cu(I) complex (Nr. 5) exhibits the largest linewidth, whereas the higher homologues such as bipyridine or o-phenanthroline do not show any copper NMR signals at all. This result is not unexpected in view of the fact that within the series of pyridine ligands the acceptor capacity increases from pyridine to o-phenanthroline.

B) Coupling Constants

From the cuprous complexes investigated in this paper samples 6, 7 and 8 (Table 1) show nuclear hyperfine interaction between copper and phosphorus. Figure 2 illustrates the well resolved quintett for $Cu[P(OCH_3)_3]_4ClO_4$ with an intensity ratio of 1:4:6:4:1. The indirect spin-spin-coupling constants between the copper isotopes and ^{31}P are summarized in Table 2 with the observed nucleus underlined. Although these large coupling constants are not unexpected, they can only be detected because of the narrow NMR lines present in these complexes (Table 1).

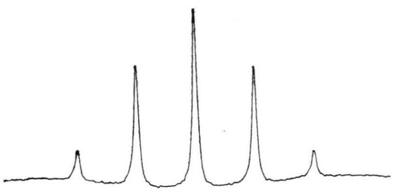

Fig. 2. ^{63}Cu FT NMR signal of a 0.08 molal solution of $Cu(I)[P(OCH_3)_3]_4ClO_4$ in $P(OCH_3)_3$ near 23.86 MHz. A spin-spin coupling constant
$J(^{63}Cu - {}^{31}P) = (1214.2 \pm 2.5)$ Hz
is derivable. The linewidth of the central line is 115 Hz. Experimental spectrum width: 10417 Hz, number of pulses: 50000, measuring time: 42 min., 350 data points were accumulated followed by 16034 points of zero-filling before Fourier transformation.

Table 2. Indirect spin-spin coupling constants of copper with ^{31}P, measured by ^{63}Cu and ^{65}Cu NMR, their Larmor frequencies are 23.86 MHz and 25.56 MHz at 2.114 T.

Sample	Coupling Constants in Hz	
	$J(^{63}Cu - {}^{31}P)$	$J(^{65}Cu - {}^{31}P)$
$Cu(I)[P(OCH_3)_3]_4ClO_4$ 0.08 molal in $P(OCH_3)_3$	1214.2 ± 2.5	1302.3 ± 3.8
$Cu(I)[P(OC_2H_5)_3]_4ClO_4$ 0.1 molal in $P(OC_2H_5)_3$	1224 ± 30	1310 ± 12

In view of the rather large coupling constants for both copper isotopes the isotope effect on J(Cu-P) was studied in greater detail. Assuming such an effect to be present the ratio $J(^{63}Cu\text{-}^{31}P)/J(^{65}Cu\text{-}^{31}P)$ is not necessarily equal to the ratio of the Larmor frequencies $\nu(^{63}Cu)/\nu(^{65}Cu)$. The determination of these Larmor frequencies has been reported in an earlier communication [11]. The value

$$\nu(^{63}Cu)/\nu(^{65}Cu) = 0.933\,523\,15(8)$$

reported in this reference is in excellent agreement with the value of

$$J(^{63}Cu\text{-}^{31}P)/J(^{65}Cu\text{-}^{31}P) = 0.932\,3(34)$$

calculated from Table 1. This result indicates that the potential isotope effect on spin-spin-coupling has to be smaller than $3.6 \cdot 10^{-3}$ for this system.

The investigations described here seem rather promising for future NMR experiments in the field of transition metal chemistry. Even in those cases where quadrupolar nuclei will dictate certain limits because of line broadening the NMR method can develop into a useful tool as demonstrated for a series of cuprous compounds.

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