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Copper-63 Nuclear Magnetic Resonance Studies of Tris(triethyl phosphite)-copper(I) Chloride in Nonaqueous Solution

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Abstract

^{63}Cu and ^{31}P NMR spectra of [CuL$_3$Cl] (L = triethylphosphite (**1**) in various nonaqueous solvents have been measured. It has been demonstrated that ligand-dissociation of **1** occurs to give [CuL$_4$]Cl (**2**) and low coordination copper(I) species. It has also been found that the formation of copper(I) species greatly depends on the solvent used. **1** and **2** give ^{63}Cu NMR signals while ^{63}Cu signals of other species are hardly observed due to significant line-broadening. By use of a dual NMR tube, **1** and **2** were determined quantitatively. It was found in a series of alcohols that **2** is preferred increasing solvent polarity. This is significantly associated with the cleavage of the Cu–Cl bond.

Introduction

It is well-known that copper(I) complexes are substitution labile in solution. Complexes of monodentate and even bidentate ligands often lead to solutions containing several species including two-, three-, and four-coordinate monomers as well as dimers, etc. In order to investigate the structure of copper(I) complexes in solution, NMR spectra have been measured and proved to be useful to characterize copper(I) complexes in solution [1, 2]. In addition to ^{1}H, ^{13}C, and ^{31}P, the ^{63}Cu NMR of the natural abundance ^{63}Cu nucleus readily provides signals having information about metal–ligand bonding [3], structure and equilibria [4] in solution. This is most available for diamagnetic copper(I) complexes. This manuscript concerns the solution equilibria of the title phosphite complex of copper(I) (**1**). Analogous complexes [5–7] of phosphines have a variety of structures such as several coordination mononuclear and binuclear complexes, the latter containing halide ion as a bridging ligand. ^{1}H and ^{13}C nuclei give poor spectra of solution samples of **1** because their spectra are complicated due to collapsing signals and/or undergoing chemical exchange averaging. On the other hand, ^{63}Cu NMR spectra are simple enough, providing useful information about the solution behavior of **1**.

Experimental

Materials

Tris(triethylphosphite)copper(I) chloride (**1**) was synthesized according to the literature [8]. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was prepared by the usual method [9]. Solvents used here were all dried and distilled before use. 80 mM solutions of **1** were prepared under highly purified nitrogen and transferred into NMR sample tube, which was utilized for both ^{63}Cu and ^{31}P NMR measurements.

Measurements

^{63}Cu NMR spectra were recorded on various solutions of **1** contained in spinning tubes (outside diameter 10 mm) on a JEOL FX 200 multinuclear spectrometer operated in the pulsed Fourier transform mode at an observing frequency of 52.92 MHz (4.7T). 4000–20000 transients were collected over a band width of 40 KHz, and free induction decay was acquired in about 8 K data points. The ^{63}Cu chemical shifts are given relative to a 50 mM solution of [Cu(CH$_3$CN)$_4$]PF$_6$ in acetonitrile at 25 °C. For obtaining the concentration of solution species, a dual tube was used with inner and outer tube diameters of 5 and 10 mm, respectively. With varying a dead time on data-acquisition, the signal intensity for broad signals was checked. Then, 100 μs was set. First, a calibration curve was made. The inner tube contained [Cu(CH$_3$CN)$_4$]PF$_6$ in CH$_3$CN as a reference sample, while various concentrations of [Cu(pyridine)$_4$]PF$_6$ in pyridine as analyzed samples were poured into the outer tube under nitrogen atmosphere. The ratio of the signal intensities of the samples to the reference sample are plotted against the concentration of copper(I) in outer tube. Figure 1 exhibits quite a good relationship.

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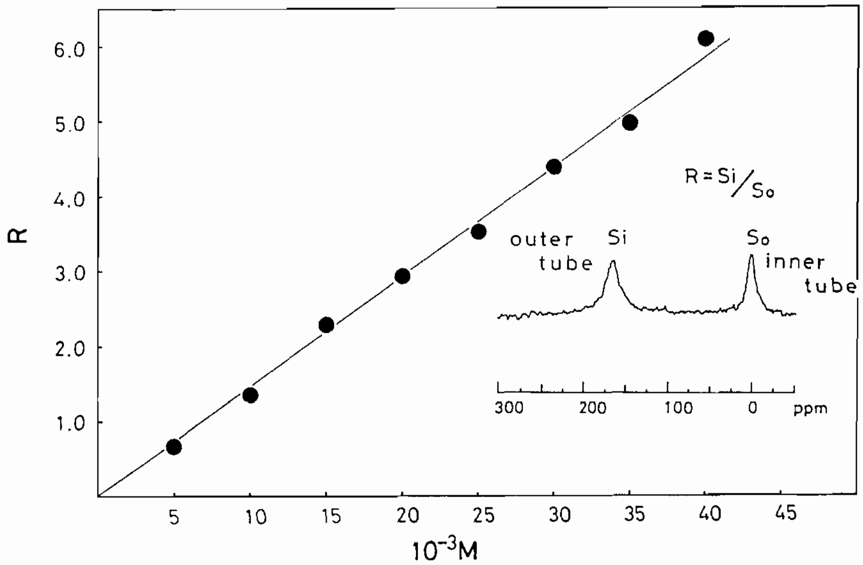

Fig. 1. Calibration curve with a dual tube system. Inner tube contains standard 0.1 M [Cu(CH_3CN)$_4$]PF_6 in CH_3CN, while outer tube contains various concentrations of [Cu(pyridine)$_4$]PF_6 in pyridine.

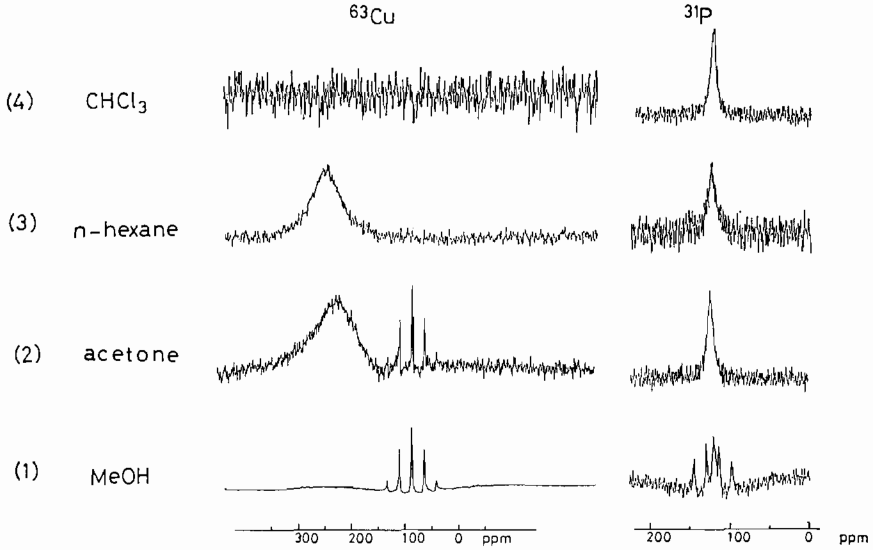

Fig. 2. ^{63}Cu and ^{31}P NMR spectra at 24 °C of solutions containing 80 mM [CuCl(P(OC_2H_5)$_3$)$_3$]. 10 mM CH_3CN solution of [Cu(CH_3CN)$_4$]PF_6 and 85% H_3PO_4 aqueous solution are external standards for ^{63}Cu and ^{31}P NMR, respectively. Solvent used is denoted at the left side of spectra.

^{31}P NMR spectra of solutions of **1** were also recorded, operating with 80.76 MHz. 10–20 × 10^3 transients were collected over a band width of 10 kHz.

Results and Discussion

Under nitrogen atmosphere **1** was dissolved in various solvents to give clear colorless solutions. No oxidation of copper(I) occurred for all the solutions. Their ^{63}Cu and ^{31}P NMR spectra are in complete agreement with those of solutions prepared from mixing CuCl and P(OC_2H_5)$_3$ (1:3 molar ratio), indicative of the lability of **1**. Typical spectra are shown in Fig. 2. ^{63}Cu NMR spectra are classified into four types according to the solvent dependence. (1) In alcohols, a sharp signal (quintet $J_{Cu-P} = 1220$ Hz) appears at 89.5 ppm, characteristic of four-coordinate [Cu(P(OC_2H_5)$_3$)$_4$]Cl (**2**). (2) In addition to a signal at 89.5 ppm, a broad signal at *ca.* 250 ppm is simultaneously detected in acetone. (3) A single broad signal appears at *ca.* 250 ppm in benzene, n-hexane, and n-heptane. (4) No signals are detected in t-butanol, 1-octanol, $CHCl_3$ and CH_2Cl_2*. On the other hand, ^{31}P NMR spectra are simple. A single broad ^{31}P signal was observed in types (2)–(4), indicating that all the species are chemically exchanged to give an averaged signal. In addition to a broad signal at 121–124 ppm, a quartet ^{31}P signal at 121 (J_{Cu-P} = 1220 Hz) of 2 is detected in type (1) (Fig. 2 (1)). This is in good agreement with that of ^{63}Cu NMR spectra. On this basis, it is concluded that 2 is free from the chemical exchange process.

The tetrahedral copper(I) complex, $[CuL_4]X$, is a highly symmetric complex which easily provides a sharp ^{63}Cu NMR signal with a linewidth at a half-height lower than 200 Hz [3, 4]. The typical example is $[Cu(P(OC_2H_5)_3)_4]Cl$ obtained here. The lower symmetry such as three- and two-coordinate forms causes effective quadrupolar relaxation [3, 4], and then the signal is much broadened or disappears due to the very large linewidth. There are no reports in the literature in which ^{63}Cu NMR spectra of trigonal and linear copper(I) complexes have been successfully detected in solution. On the other hand, a tetrahedral copper(I) complex, even if in a ternary ligand system, possibly gives a detectable signal. Cubane complex, $[Cu(CO)(t\text{-}BuO)]_4$, gave a rather broad ^{63}Cu signal at 49 ppm [10]. In this complex, each copper has coordinated three oxygen atoms and one carbon atom, and thus is tetrahedral. On this basis, 1 is also an observable species. Then, we can assign a ^{63}Cu signal at 250 ppm to 1 (Fig. 2 (2) and (3)). Some averaging of this broad signal may occur due to the chemical exchange with the lower symmetry species, because this signal linewidth shows the solvent dependence.

In the case of phosphine, the equilibria in $CHCl_3$ of [Cu(phosphine)$_3$X] (X = Cl, Br, and I) have been examined [5–7], and the dissociation of the precursor into the lower coordination mononuclear and binuclear complexes has been determined. Some of equilibria are presented as follows:

$$L_3CuCl\,(1) + L \rightleftharpoons [CuL_4]\,Cl\,(2) \qquad (1)$$

$$L_3CuCl\,(1) \rightleftharpoons L_2CuCl\,(3) + L \qquad (2)$$

$$L_2CuCl\,(3) \rightleftharpoons LCuCl\,(4) + L \qquad (3)$$

$$2L_2CuCl\,(3) \rightleftharpoons L_4Cu_2Cl_2\,(5) \qquad (4)$$

Among these species, 3–5 cause the disappearance of ^{63}Cu NMR signals, while 1 and 2 provide detectable signals. Because a marked difference in ^{63}Cu NMR spectra has been found for various solutions of 1, it is to be noted that these equilibria are greatly influenced by the solvent used. How does a difference in solvent give rise to the variety of equilibria?

It is interesting that four-coordinate 2 preferably forms in methanol (Fig. 2(1)). Upon dissolution of 1, $P(OC_2H_5)_3$ existing in solution is at most three times the equivalent of copper which comes from the dissociation of 1 (eqns. (2) and (3)). It is to be emphasized that ^{63}Cu NMR spectra show a signal of 1 as a principal species even in neat $P(OC_2H_5)_3$. Accordingly, the concentration of $P(OC_2H_5)_3$ is not a serious factor influencing equilibria for the $CuCl/P(OC_2H_5)_3$/alcohol system. In alcohol, the dissociation of both $P(OC_2H_5)_3$ and Cl^- is involved in the formation of 2. Especially, the cleavage of Cu–Cl is an important step in order to form 2 (eqn. (1)). The coordination of alcohol may be considered, because alcohol is often a good ligand [11]. t-Butanol not only has a bulky group, which hinders its coordination to copper(I), but also has low polarity. In order to elucidate which is the most effective factor, coordinating ability or bulk properties of alcohol, 1-octanol was used as solvent. 1-Octanol is the least polar among the alcohols used here, but it has much more coordinating ability than t-butanol because it has no serious steric hindrance. A signal of 2 was not found in either 1-octanol or in t-butanol. We have previously demonstrated that the copper(I)–halide bond is hardly cleaved in a non-polar solvent [12] for the CuCl/2,2′-bipyridine system. In order to substantiate this for the $CuCl/P(OC_2H_5)_3$ system, 2 was quantitatively determined in various alcohols. The percentage of 2 to total amount of copper was obtained and plotted against the specific dielectric constant (ϵ) [13] of alcohol (Fig. 3). Figure 3 reveals quite a good relationship between them, indicating that polar properties promote the formation of 2. Hence, the polarity of alcohol is significantly important for the formation of 2. In alcohols with low polarity, dissociation of the chloride ion

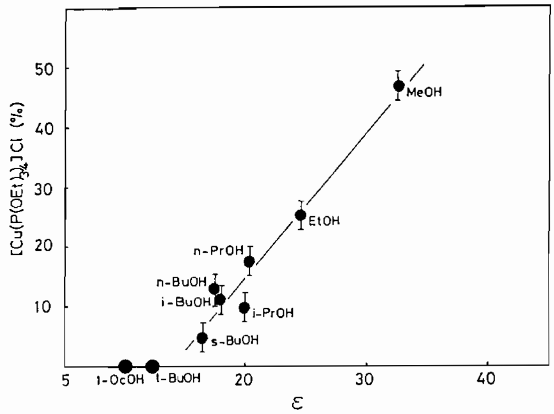

Fig. 3. A plot of the percentage of $[Cu(P(OC_2H_5)_3)_4]Cl$ to total copper(I) *vs.* specific dielectric constant of alcohol.

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*Very small amounts of 2 were detected.

hardly occurs, and thus 2 is the minor species, and a low symmetry complex is favored, with which chloride ion is significantly associated. Even the most polar methanol cannot provide complete formation of 2, where nearly 50% is produced (Fig. 2). Accordingly, the Cu–Cl bond is significantly stable, which is attributed to the ionic nature of the Cu^+–Cl^- bond. The molar conductivity of the methanol solution of 1 is 40 ohm^{-1} cm^2 mol^{-1} (18 °C), which is nearly half the value of the standard 1:1 electrolyte (80–115 ohm^{-1} cm^2 mol^{-1}) [14]. 50% of the chloride ion dissociates and another 50% binds copper. This is in good agreement with the result obtained from the ^{63}Cu NMR spectrum.

In the case of acetone, the ratio of 2 to 1 is 0.13% (Fig. 2) and the ratio of 2 to total copper is only 0.026. It is to be noted that the polarity of acetone makes 1 and 2 coexist in solution, but not as principal species. In type (3), 2 was not detected, and the quantity of 1 has been determined in a similar way. The percentage to total copper is, for example, 69% for n-hexane. The residual species are ascribed to the lower symmetry ones. These species have Cu–Cl bonds because the molar conductivities of these solutions gave no 1:1 electrolyte value; the value was below the limit of detection. It is understood that cleavage of the Cu–Cl bond hardly occurs, which is also associated with the bulk properties of type (3) and (4) solvents.

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References

1 S. Kitagawa, M. Munakata and N. Miyaji, *Inorg. Chem., 21,* 3842 (1982).
2 M. Munakata and S. Kitagawa, in D. K. Karlin and J. Zubieta (eds.), 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives', Academic Press, New York, 1983, Chap. 23.
3 S. Kitagawa and M. Munakata, *Inorg. Chem., 23,* 4388 (1984).
4 (a) T. Yamamoto, H. Haraguchi and S. Fujiwara, *J. Phys. Chem., 74,* 4369 (1970); (b) O. Lutz, H. Oehler and P. Kroneck, *Z. Naturforsch., Teil A., 33,* 1021 (1978); (c) U. Ochsenbein and C. W. Schlaepfer, *Helv. Chim. Acta, 63,* 1926 (1980); (d) P. Kroneck and J. Kodweiss, *Z. Naturforsch., Teil A, 37,* 186 (1982).
5 D. J. Fife, W. M. Moore and K. W. Morse, *Inorg. Chem., 23,* 1684 (1984).
6 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem., 15,* 1155 (1976).
7 S. J. Lippard and J. J. Mayerle, *Inorg. Chem., 11,* 753 (1972).
8 J. C. Bommer and K. W. Morse, *Inorg. Chem., 22,* 592 (1983).
8 D. F. Shriver, in 'Inorganic Syntheses', Vol. 19, Wiley-Interscience, New York, 1979, p. 90.
10 R. L. Geerts, J. C. Huffman, K. Folting, T. H. Lemmen and K. G. Caulton, *J. Am. Chem. Soc., 105,* 3503 (1983).
11 M. Munakata, S. Kitagawa and M. Miyajima, *Inorg. Chem., 24,* 1638 (1985).
12 (a) S. Kitagawa and M. Munakata, *Inorg. Chem., 20,* 2261 (1981); (b) S. Kitagawa, M. Munakata and S. Okada, *Bull. Chem. Soc. Jpn., 55,* 3491 (1982).
13 J. A. Riddick and W. B. Bunger, 'Organic Solvent', Wiley-Interscience, New York, 1970.
14 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).