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CP/MAS NMR studies on binding environment of CH_3CN in Cu(I) complexes with disilane-bridged bis(methylpyridine) ligands†

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CP/MAS NMR spectroscopies have developed as an important tool for studying the structure in the crystalline state. In this work, the structures of representative Cu(I) complexes **1–3** with disilane-bridged bis(methylpyridine) ligands in the crystalline state were investigated by CP/MAS NMR. ^{13}C CP/MAS NMR confirmed the presence of CH_3CN in the crystals of **2** and **3**, but the environment around CH_3CN could not be determined. Natural abundance (*ca.* 0.36%) ^{15}N CP/MAS NMR measurements could confirm the difference of CH_3CN environment between coordinating solvent in **2** and crystal solvent in **3**. The ^{15}N CP/MAS of CH_3CN in **3** shows a singlet because it is not coordinated to Cu(I) and the crystal structure is stabilized by multiple intermolecular interactions. These data have provided valuable information on Cu(I) coordination environment, which was in good accordance with single-crystal X-ray analysis.

Introduction

Flexible molecular structures are known to induce crystalline polymorphism. The transition between the stable and metastable polymorphs triggered through external stimuli can induce alternation of photophysical properties.[1,2] Among them, investigations on the relationship between structure and properties of Cu(I) complexes are of significant interest.[3–6] Copper(I) complexes have been shown to be excellent candidates for solid-state emitters due to their high earth-abundance and low cost, coupled with their ability of bright luminescence at rt, resulting in complexes with interesting photophysical characteristics. These compounds have been found to exhibit a variety of structures from mononuclear to polynuclear copper complexes. Recently, we reported the synthesis and photophysical properties of Cu(I) complexes with disilane-bridged dipyridine ligands. Some compounds showed responsiveness under external stimuli in the crystalline state.[7]

Solid-state NMR is a non-destructive measurement method, and various information can be obtained by the measurement.[8–12] Especially, CP/MAS NMR spectroscopy can provide information about the structure and bonding of metal complexes in the crystalline state. Recently, the techniques have been developed to improve resolution by rotating at high speeds.[13] ^{13}C and ^{15}N CP/MAS NMR, along with single-crystal X-ray structure analysis, are powerful techniques for structural analysis.[14–17]

The major difficulty in employing ^{15}N NMR spectroscopy lies in its sensitivity, which is very low due to the low natural abundance (0.36%) of the ^{15}N isotope. Although nitrogen-15 labelling compounds were used to employ ^{15}N CP/MAS NMR, ^{15}N NMR can be measured even for unlabelled ^{15}N compounds by increasing accumulation numbers and using high-resolution NMR. Recently, we measured ^{15}N CP/MAS NMR to track structural changes of organosilicon compounds upon mechanical stimulation.[18]

Cu complexes often decompose in solution, requiring solid-state NMR measurements. Previously, we reported the synthesis and optical properties of several Cu(I) complexes.[19] The ^{13}C CP/MAS NMR of **2** and **3** showed the peaks of CH_3CN as similar chemical shift, and it was impossible to distinguish existence state between the crystal solvent and coordinated ligand. ^{15}N CP/MAS NMR of transition metal complexes were measured to distinguish binding mode of CH_3CN. As Cu(I) complex, several ^{15}N CP/MAS NMR of Cu(I) complexes were reported in natural abundance.[20–23] However little clear evidence has been given on the effect of metal binding to the ^{15}N nuclear shielding constants.[24–27] In this paper, we used natural abundance ^{15}N CP/MAS NMR to study binding mode of CH_3CN in Cu(I) complexes **1–3** (Fig. 1).

Experimental section

Materials

All chemicals and reagents were obtained from commercial sources and used without additional purification.

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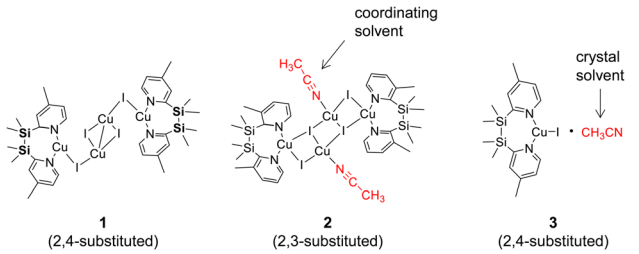

Fig. 1 Chemical structures of copper complexes **1–3** studied in this work.

1,1,2,2-Tetramethyl-1,2-bis(4-methylpyridin-2-yl)disilane and 1,1,2,2-tetramethyl-1,2-bis(3-methylpyridin-2-yl)disilane were prepared according to our previous report.[7]

Synthesis of 1

CuI (380 mg, 2.0 mmol) and 1,1,2,2-tetramethyl-1,2-bis(4-methylpyridin-2-yl)disilane (300 mg, 1.0 mmol) were dissolved in CH_3CN (40 mL) at rt. The resulting yellow mixture was stirred at rt for 12 h. The solvent was evaporated under reduced pressure and the residue was washed with diethyl ether to give **1** as pale yellow crystalline solid. The solid was recrystallized from CH_3CN to obtain analytically pure complex **1** as colorless cubes. Yield: 42% (290 mg). Elemental analysis. Calcd for $C_{32}H_{48}N_4Cu_4I_4Si_4$: C, 28.20; H, 3.55; N, 4.11. Found: C, 28.47; H, 3.53; N, 4.24.

Synthesis of 2

CuI (380 mg, 2.0 mmol) and 1,1,2,2-tetramethyl-1,2-bis(3-methylpyridin-2-yl)disilane (300 mg, 1.0 mmol) were dissolved in CH_3CN (40 mL) at rt. The resulting yellow mixture was stirred at rt for 12 h. The solvent was evaporated under reduced pressure and the residue was washed with diethyl ether to give **2** as pale yellow crystalline solid. The solid was recrystallized from CH_3CN to obtain analytically pure complex **2** as yellow cubes. Yield: 44% (305 mg). Elemental analysis. Calcd for $C_{36}H_{54}N_6Cu_4I_4Si_4$: C, 29.92; H, 3.77; N, 5.82. Found: C, 29.76; H, 3.70; N, 5.78.

Synthesis of 3

CuI (190 mg, 1.0 mmol) in CH_3CN (15 mL) was added dropwise to a solution of 1,1,2,2-tetramethyl-1,2-bis(4-methylpyridin-2-yl) disilane (300 mg, 1.0 mmol) in CH_3CN (5 mL) over 5 min at rt. After stirring at rt for 10 min, **3** was obtained as a yellow crystalline solid (314 mg, 60%). The solid was recrystallized from CH_3CN to obtain analytically pure complex **3** as colorless cubes. The spectroscopic data were identical to our previous reported data.[19]

Single-crystal X-ray structural analyses

All single-crystal Xray diffraction measurements were conducted using a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a rotating-anode generator. Each crystal was mounted on a loop using paraffin oil. Diffraction data were collected at around 100 K and processed using the Crystal Clear program. Structures were solved by direct methods using SIR-2011. Structural refinements were conducted by the full-matrix least-squares method using SHELXL-2013. All non-H atoms were refined anisotropically, and all H atoms were refined using the riding model. All calculations were performed using the Crystal Structure crystallographic software package. The crystallographic data were deposited in the Cambridge Crystallographic Data Centre.

Crystallographic data for 1

$C_{32}H_{48}Cu_4I_4N_4Si_4$, crystal dimensions: 0.15 mm × 0.15 mm × 0.05 mm. M = 1362.86, monoclinic, $P12_1/n1$, a = 9.8145(5) Å, b = 14.0010(8) Å, c = 16.7363(10) Å, α = 90°, β = 98.366(2)°, γ = 90°, V = 2275.3(2) Å^3, Z = 2, T = 109 K, D_{calc} = 1.989 g cm^{-3}, F_{000} = 1304.0, λ = 0.71073 Å (Mo Kα), μ = 4.690 mm^{-1}, R_1 = 0.0177 ($I > 2\sigma(I)$), wR_2 = 0.0462 (all data). GOF = 1.063. CCDC 2419410.

Crystallographic data for 2

$C_{36}H_{54}Cu_4I_4N_6Si_4$, crystal dimensions: 0.15 mm × 0.15 mm × 0.05 mm. M = 1444.97, triclinic, $P\bar{1}$, a = 9.3981(5) Å, b = 10.1021(6) Å, c = 14.9219(8) Å, α = 81.667(2)°, β = 74.599(1)°, γ = 64.227(1)°, V = 1229.25(12) Å^3, Z = 1, T = 112 K, D_{calc} = 1.952 g cm^{-3}, F_{000} = 696.0, λ = 0.71073 Å (Mo Kα), μ = 4.348 mm^{-1}, R_1 = 0.0340 ($I > 2\sigma(I)$), wR_2 = 0.0706 (all data). GOF = 1.036. CCDC 2419411.

Crystallographic data for 3

$C_{18}H_{27}CuIN_3Si_2$, crystal dimensions: 0.15 mm × 0.13 mm × 0.05 mm. M = 532.04, orthorhombic, $Pca2_1$, a = 16.7137(6) Å, b = 10.0411(3) Å, c = 13.9102(5) Å, α = 90°, β = 90°, γ = 90°, V = 2334.46(14) Å^3, Z = 4, T = 100 K, D_{calc} = 1.514 g cm^{-3}, F_{000} = 1064.0, λ = 0.71073 Å (Mo Kα), μ = 2.367 mm^{-1}, R_1 = 0.0221 ($I > 2\sigma(I)$), wR_2 = 0.0431 (all data). GOF = 1.033. CCDC 2339248.

CP/MAS NMR spectroscopy

The sample was packed into a 4 mm zirconia rotor and measured with ^{13}C and ^{15}N cross-polarization/magic angle spinning (CP/MAS) NMR using a spectrometer (Bruker AVANCE III HD 600WB) at a Larmor frequency of 150.97 MHz (^{13}C) and 60.86 MHz (^{15}N). Bruker MAS probe head (MAS4DR) was used with a HR-MAS rotor with 4 mm diameter (HZ05538) and Teflon insert (50 μL), and sample spin rates were 10 kHz for ^{13}C and 8 kHz for ^{15}N, respectively. The chemical shifts refer to tetramethylsilane (^{13}C) and nitromethane (^{15}N) at 0.00 ppm. Glycine was used as a second reference material for ^{13}C NMR, and its carbonyl signal was set at 176.46 ppm. NH_4Cl (10 atom% ^{15}N) was used as a second reference material for ^{15}N NMR, which was set at −341.15 ppm. The samples were measured at ambient probe temperature.

Results and discussion

The ^{13}C CP/MAS NMR can be used to correlate solution NMR data and X-ray structure data.[28] ^{13}C CP/MAS NMR and X-ray

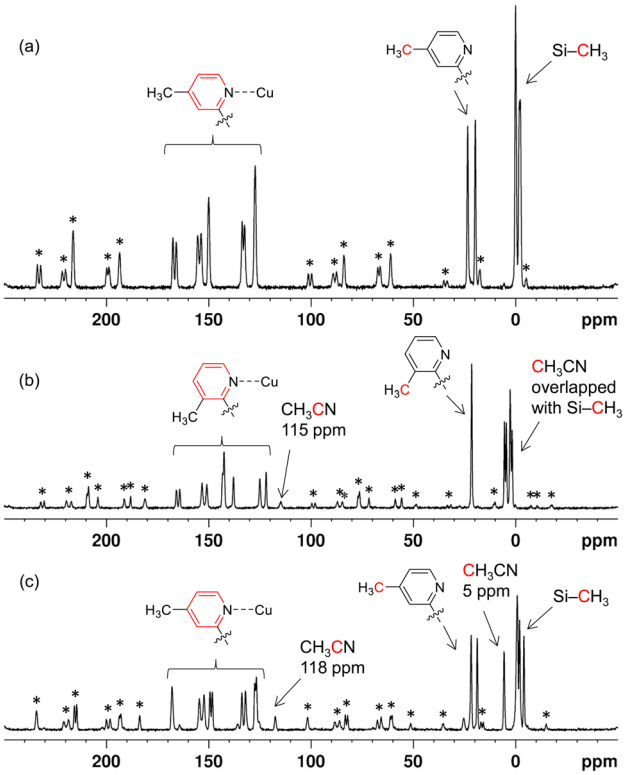

Fig. 2 ^{13}C CP/MAS NMR (151 MHz, 10 kHz MAS). (a) **1**, (b) **2**, and (c) **3**. The parameters of CP/MAS are as follows: CP contact time: 2 ms, recycle delay: 8 s, and the number of scans: 2000. The signals with asterisks indicate spinning side band.

analysis are shown in Fig. 2 and S1,† respectively. Chemical shifts are sensitive to the surrounding environment, and hence obvious changes can be found in different structures. In the solid-state spectra of copper complex **1**, we observed a number of peaks than the number of chemically distinct carbon atoms in the molecules (Fig. 2(a)). The doublet-like signals with the intensity ratio of *ca.* 1 : 1 observed in some peaks of ^{13}C CP/MAS NMR spectra arise due to structurally nonequivalent carbon of the complex in the unit cell.

^{13}C CP/MAS NMR reflects the unsymmetrized ligand molecule by crystallization and CH_3CN molecules. ^{13}C CP/MAS of **2** shows signals of CH_3CN at 115 ppm (CH_3CN) and around 5 ppm (CH_3CN, overlapped with Si–CH_3) (Fig. 2(b)). The signal at 118 ppm and 5 ppm is attributed to the ^{13}C peaks of CH_3CN in the crystal of **3** (Fig. 2(c)). However, ^{13}C CP/MAS NMR did not show obvious information based on structural differences on CH_3CN between **2** and **3**.

Nitrogen is a constituent of many ligands which are important in coordination chemistry. Natural abundance ^{15}N CP/MAS NMR has been reported as a novel tool for investigating molecular information. Particularly, it is possible to consider the structure of metal complexes, and the ^{15}N chemical shifts are sensitive to the coordinating or uncoordinating N atoms. Therefore, we measured ^{15}N CP/MAS NMR of these copper complexes **1**–**3**.

When the ^{15}N NMR of copper complex **1** without CH_3CN was measured in the crystalline state, multiple peaks were observed

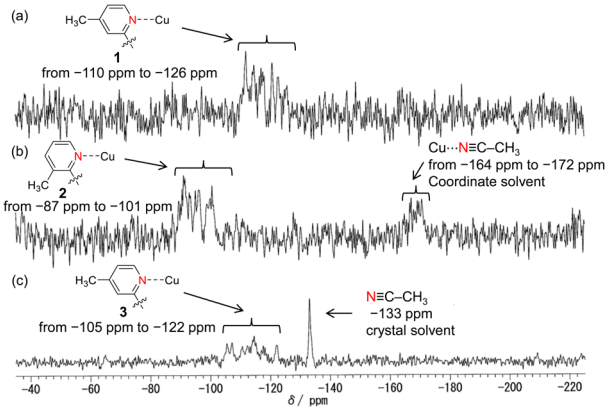

Fig. 3 Natural abundance ^{15}N CP/MAS NMR (61 MHz, 8 kHz MAS). (a) **1**, (b) **2**, and (c) **3**. The parameters of CP/MAS are as follows: CP contact time: 5 ms, recycle delay: 10 s, and the number of scans: (a) 8000, (b) 12 000, and (c) 12 000.

at from −110 ppm to −126 ppm, which were assigned as ^{15}N of pyridine moiety (Fig. 3(a)). The ^{15}N chemical shift was consistent with the results in analogous systems in solution.[29–33] ^{15}N resonance of the free pyridine-based ligand showed at around −70 ppm while the coordination of the pyridine to Cu(I) in solution showed the resonance at around −100 ppm in the ^{15}N NMR.[34] The complicated peaks in the solid state are due to not only the unsymmetrization observed in ^{13}C spectra but also coupling between ^{15}N and ^{63}Cu/^{65}Cu nuclei. In a similar system, ^{31}P CP/MAS NMR of Cu(I) complexes having phosphine ligands show complicated peaks due to coupling between the ^{31}P and ^{63}Cu/^{65}Cu.[35,36]

Complexes **2** and **3** contain one CH_3CN, which exist in different states in the crystal. ^{15}N NMR chemical shifts are sensitive to the environment of N moiety. Therefore, detectability of CH_3CN in crystals is discussed by CP/MAS ^{15}N NMR for identifying specific chemical functional groups.

^{15}N CP/MAS NMR of **2** was shown in Fig. 3(b). The multiple peaks from −87 ppm to −101 ppm were ^{15}N chemical shifts of pyridine ligands in **2**. The chemical shift moved to the downfield side in comparison with **1** are due to the difference in the substitution position of the methyl group on pyridine ring. The ^{15}N resonance of CH_3CN in **2** was also observed as multiple peaks from −164 ppm to −172 ppm. The chemical shift in the characteristic ^{15}N resonance was observed upon *N*-cyano coordination to Cu(I) *via* Cu···N≡C–CH_3 interactions.

CP/MAS ^{15}N NMR of **3** was measured (Fig. 3(c)). The multiple peaks from −105 ppm to −122 ppm were assigned to ^{15}N of pyridine ring coordinated to Cu(I). ^{15}N peak of CH_3CN molecules as the crystal solvent was observed at −133 ppm as a sharp peak, which was lower field relative to **2**. The CH_3CN peak of **3** is sharp because CH_3CN molecules have no Cu···N interaction in the crystalline state. Although these results on CH_3CN binding mode agree with X-ray structures of **2** and **3**, single crystal X-ray determinations are not always available for analysing the structure. The structures can often not be determined by Rietveld analysis of microcrystals. There is a need for alternative

spectroscopic methods to determine the ligand coordination mode. ^{15}N CP/MAS NMR is a valuable tool for distinguishing the binding environments in the crystals. This study provides spectroscopic support for insight into the coordination mode of solvent in metal complexes.

CH_3CN molecules in **2** exist in the crystal through a coordination bond with Cu(I) ($CH_3C{\equiv}N\cdots Cu$), and CH_3CN molecules in **3** exist through hydrogen bonds between N lone pair of CH_3CN and aromatic proton ($CH_3C{\equiv}N\cdots H$–Ar) (Fig. S2†). The ^{15}N NMR peak shapes of CH_3CN change depending on the coordination or uncoordination with Cu(I). ^{15}N NMR peaks of CH_3CN in **2** are complicated by the coupling between ^{15}N and $^{63/65}$Cu nuclei due to the coordination of CH_3CN to Cu(I). On the other hand, there is no interaction between CH_3CN and Cu(I) in the crystal of **3**, and ^{15}N NMR peak of CH_3CN is observed as a sharp singlet.

Conclusion

This work describes detailed structural information on Cu(I) complexes in the crystalline state using natural abundance ^{15}N CP/MAS NMR. ^{13}C and ^{15}N CP/MAS NMR spectra of **1–3** were in accord with the direct structural data on the complexes. CH_3CN in these complexes has restricted molecular motion in single crystals and could be observed by CP/MAS NMR.[37] Natural abundance ^{15}N CP/MAS NMR spectra provided considerable information on the crystalline state, because the state of the solvents contained can be deduced from NMR spectroscopy in addition to single crystal X-ray structure analysis. ^{15}N NMR peak shapes of these Cu(I) complexes are related to the environment of the nitrogen atoms in the crystal. The differences between coordinated and uncoordinated CH_3CN were able to be distinguished by ^{15}N CP/MAS NMR. Molecular packing had an impact on the splitting patterns and peak shapes of the ^{15}N peak of CH_3CN.

The ^{15}N chemical shift and peak shape were sensitive to cyanide interactions observed in Cu(I) complexes. Sharp ^{15}N signal was observed corresponding to CH_3CN of crystal solvent with the stabilization of multiple intermolecular interactions. On the contrary, multiple ^{15}N signals of CH_3CN was observed corresponding to $Cu\cdots N{\equiv}C$–CH_3 interactions. These observations suggest a detailed study of solvent environments in the crystal.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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