

³¹P CPMAS NMR Studies Of Some Mono- and Di-Nuclear complexes of Copper (I) Iodide and Phosphines

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Abstract

Phosphorus-31 CPMAS spectra are reported for some copper(I) iodide phosphine complexes showing monomeric and dimeric structures. The spectra show distorted quartets of unequal line spacing, indicating significant deviation from spherical symmetry at the copper nucleus. A larger quadrupole induced distortion is observed for the three-coordinate monomeric complexes than that for the four-coordinate dimeric complexes.

Keywords: Copper (I) iodide phosphine complex, ³¹P CPMAS NMR, monomeric copper complex, dimeric copper complex

Résumé

Nous présentons les spectres CPMAS du phosphore-31 pour quelques complexes iodure de cuivre (I) phosphine qui montrent les structures monomères et dimères. Les spectres montrent des bandes quadruples déformées avec espacements inégaux, indiquant une déviation significative de la symétrie sphérique au noyau de cuivre. Une plus grande distorsion quadripolaire induite peut être observée pour les complexes à triple coordinance par rapport à celle des complexes dimères à quadruple coordinance.

Introduction

The aggregation of closed shell d¹⁰ metals, particularly copper (I), leads to mono and polynuclear coordination compounds with diverse solid state structures (1-3). This structural richness is accompanied by interesting photophysical properties, making them potential candidates for applications in materials science (4-7). In this context, copper (I) halides react with monodentate phosphine ligands to yield two, three and tetra coordinate complexes with different stoichiometries. Within

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the (1:2) stoichiometry, CuI(PR₃)₂ complexes have been shown to exhibit a monomeric, three coordinate structure (8), in addition to the dimeric four coordinate structure. The latter situation was reported for the ligands PH₂Ph, PMePh₂, PMe₃ and P(C₂Ph)₃ (9-12).

In the absence of good single crystals to obtain quality X-ray diffraction structures for the complexes, we have investigated the possibility of utilizing NMR data in the solid state for possible differentiation between monomeric three coordinate structures and dimeric four coordinate structures. In this work, a number of substituted phosphines ligands complexed with CuI will be characterized using solid state NMR. ³¹P solid state NMR spectra provide useful structural and molecular information. Cu nuclei are quadrupolar and the use of solid state NMR allows the connection of structural and molecular properties such as bond distances and bond angles, ⁶³Cu quadrupole coupling constant, and location of the electric field gradient at the copper atom with respect to the molecular frame.

Experimental

Synthesis of the complexes

For the complexes, [CuI(P(C₆H₁₁)₃)₂], [CuI(PH(C₆H₁₁)₂)₂], [CuI(P(C₆H₅)₂C₆H₁₁)₂] and [CuI(P(C₆H₅)₂CH=CH₂)₂], synthesis, elemental analyses and IR data were reported earlier (13). However, single crystal X-ray data is presented only for the complex [CuI(P(C₆H₁₁)₃)₂].

The complex [CuI(P(C₆H₅)₂*i*-Pr)₂]₂ was prepared as follows.

A suspension of 300 mg (1.3 mmol) of isopropylidiphenylphosphine and 500 mg (2.6 mmol) of copper (I) iodide in 50 mL of isopropanol was refluxed for 16 hours. The resulting solution was filtered while hot. The slow evaporation of the solvent at room temperature resulted in a crystalline product containing single crystals suitable for X-ray diffraction analysis. Satisfactory C, H elemental analysis was obtained. IR (KBr) 3047, 2856, 2957, 1460, 1432, 1261, 1184, 1153, 1098, 1026, 802,

741, 696, 515 cm^{-1} . The details of the single crystal X-ray diffraction data is reported separately (14) and it showed that the two iodine atoms form a bridging structure.

Solid state NMR

Solid state cross-polarization magic-angle spinning (CP/MAS) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained at ambient temperature on a JEOL Lambda 500 spectrometer operating at a frequency of 202.35 MHz. Contact time of 3 ms was used with a proton pulse width of 6 μs , with a recycle delay of 10 s. The samples were packed in zirconia rotors and spun at around 5 kHz at the magic angle. Approximately 1000 FID's were collected and transformed with a line broadening of 10 Hz. Chemical shifts were referenced using an external sample of solid PPh_3 , which has a shift of -9.9 ppm with respect to 85% H_3PO_4 .

Results and Discussion

Of the five complexes studied in this work, X-ray single crystal structure is reported for only the two complexes, $[\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2]$ which shows a monomeric three coordinate structure, and $[\text{CuI}(\text{P}(\text{C}_6\text{H}_5)_2i\text{-Pr})_2]_2$ which shows a dimeric four coordinate structure. The structural data for these two complexes are compiled in Table 1.

The ^{31}P CPMAS spectra of Cu-phosphine complexes exhibit asymmetric quartets, where the three line-spacings are not constant. This phenomenon is due to the

combination of scalar J coupling with incompletely averaged dipolar coupling between phosphorus nucleus (^{31}P , nuclear spin $1/2$) and copper nucleus (^{63}Cu , ^{65}Cu , nuclear spin $3/2$), anisotropic J interactions and copper nuclear quadrupole coupling (Figure 1) (15,16).

The line-widths are such that the two quartets are not resolved and the observed spectrum is dominated by the ^{63}Cu (natural abundance 69.09%). If the line-widths are sufficiently narrow, the ^{65}Cu (natural abundance 30.91%) coupling is identified by a splitting of the outer peaks of the quartet. In our case only one quartet was observed for the four monomeric complexes $[\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2]$, $[\text{CuI}(\text{PH}(\text{C}_6\text{H}_{11})_2)_2]$, $[\text{CuI}(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_{11})_2]$ and $[\text{CuI}(\text{P}(\text{C}_6\text{H}_5)_2\text{CH}=\text{CH}_2)_2]$. Figure 2a shows a typical case for $[\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2]$. However, in the case of the dimeric complex $[\text{CuI}(\text{P}(\text{C}_6\text{H}_5)_2i\text{-Pr})_2]_2$, we observed two quartets of equal intensity (Figure 2b), which were fairly well resolved. Unfortunately, ^{31}P NMR alone cannot distinguish between monomeric and dimeric complexes, because the non-equivalence of phosphorus could arise even in the monomeric complexes, if either the two phosphine ligands in the molecule are crystallographically different or there are two crystallographically different molecules in a unit cell. However, for the dimer, $[\text{CuI}(\text{P}(\text{C}_6\text{H}_5)_2i\text{-Pr})_2]_2$, the X-ray structure shows (14) that the two P atoms on Cu are different from the other two P atoms on the other Cu due to different Cu-P distances. This is further corroborated by observing two quartets in the ^{31}P spectrum. The chemical shifts and the line spacing for the quartets are given in Table 2 along with

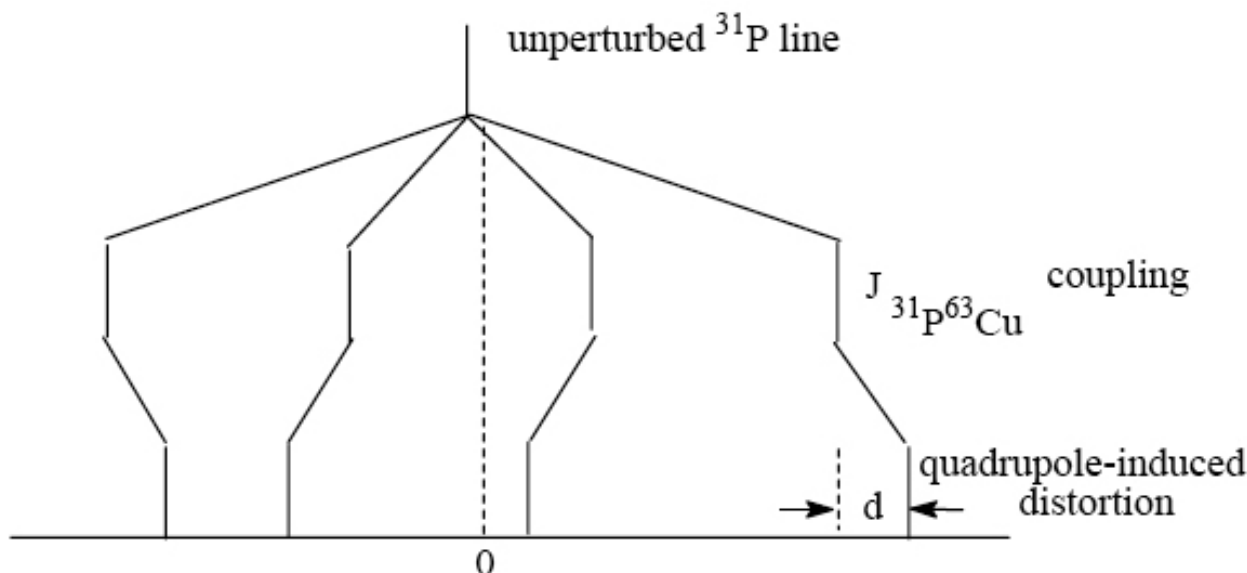


Figure 1. Scheme corresponding to a ^{31}P solid-state NMR quartet showing the combined effects of isotropic J(P,Cu) scalar coupling and the quadrupole-perturbed dipolar and anisotropic anisotropic scalar couplings (d).

Table 1. Selected bond lengths (Å) and bond angles(°).

Bond Distances		Bond Angles	
For [CuI(P(C ₆ H ₁₁) ₃) ₂]			
Cu-I	2.487 (3)	P-Cu-I	112.2 (1)
Cu-P	2.285 (3)	P-Cu-P	135.5 (1)
P-C	1.864 (9)		
P-C	1.871 (9)		
For [(PPr ^t Ph ₂) ₂ CuI] ₂			
Cu1-P1	2.2849 (7)	P2-Cu1-P1	116.29 (3)
Cu2-P2	2.2760 (8)	P1-Cu1-I1	112.38 (2)
Cu1-I1	2.6498 (4)	P2-Cu1-I1	119.70 (2)
Cu1-I1 ^a	2.8393 (4)	P1-Cu1-I1	100.10 (2)
P1-C1	1.826 (3)	P2-Cu1-I1	108.36 (2)
P1-C7	1.827 (3)	I1-Cu1-I1	95.562 (11)
P1-C13	1.854 (3)	Cu1-I1-Cu1	84.438 (11)
P2-C16	1.827 (3)	C1-P1-C7	105.43 (12)
P2-C22	1.830 (3)	C1-P1-C13	102.56 (12)
P2-C28	1.861 (3)	C7-P1-C13	104.71 (12)
		C1-P1-Cu1	119.79 (9)
		C7-P1-Cu1	110.24 (9)
		C13-P1-Cu1	112.80 (9)
		C16-P2-C22	104.59 (13)
		C16-P2-C28	104.94 (13)
		C22-P2-C28	101.32 (13)
		C16-P2-Cu1	110.78 (9)
		C22-P2-Cu1	120.16 (9)
		C28-P2-Cu1	113.55 (10)

data for another dimeric four coordinate Cu-phosphine complexes for comparison.

The first-order analysis (justified at high magnetic field of 11.7 tesla used in our experiments) predicts the outer two lines to shift upfield and the inner two lines to shift downfield by a magnitude d such that $\Delta v_2 - \Delta v_1 = \Delta v_3 - \Delta v_2 = 2d$, from which $d = (\Delta v_3 - \Delta v_1)/4$. The Δv_2 is equal to $^1J_{\text{Cu-P}}$. The divergence of the ratio $\Delta v_3/\Delta v_1$ from unity is approximately proportional (6) to the copper nuclear quadrupole coupling constant, e^2qQ . The large $\Delta v_3/\Delta v_1$ values observed in these complexes indicate significant deviation from spherical symmetry at the copper nucleus. The observed values of $\Delta v_3/\Delta v_1$ are in the range 1.1-1.3, and is consistent with the coordination number 3 as reported (17) for other phosphine complexes.

Multiplication of d by the ^{63}Cu Zeeman frequency yields a field independent parameter dv_{Cu} that is suitable for comparing results obtained from spectra recorded at different field strengths.

The first order theory generates the equation (1) (15):

$$dv_{\text{Cu}} = -(3\chi/20)(D-\Delta J/3)(3\cos^2\beta - 1 + \eta\sin^2\beta\cos 2\alpha) \quad (1)$$

where, χ is the quadrupole coupling constant, η is the asymmetry parameter of electric field gradient at copper, $\Delta J = J_{\parallel} - J_{\perp}$, D is the dipolar coupling in kHz, which is $12.9/r^3$ where r is the Cu-P distance in angstroms, β and α are the polar and azimuthal angles which fix the location of the Cu-P internuclear vector in the principal axis system of the quadrupolar tensor. Olivieri (15) has used $\Delta J = +0.6$ kHz and $\eta = 0.3$ in a series of phenylphosphine complexes of the type P_2CuX with success in predicting the d values. We have used the same values for ΔJ and η , to calculate χ in $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ from the experimental d value and found it to be -55.4 MHz. This value is in the range reported (15) for other phosphine complexes of the type P_2CuX . As can be seen from Table 2, it can be safely concluded that the three complexes, not characterized by X-ray studies, show close resemblance to

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