

Anisotropy in the ^{31}P , $^{63/65}\text{Cu}$ Indirect Spin–Spin Coupling and ^{31}P Nuclear Shielding Tensors of Linear Copper(I) Phosphines

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Phosphorus-31 CP/MAS NMR spectra of two linear bis(tribenzylphosphine)cuprate(I) salts reveal significant anisotropy in the one-bond ^{31}P , $^{63,65}\text{Cu}$ J tensors. The parallel and perpendicular components of $^1J(^{31}\text{P}, ^{63}\text{Cu})$, for example, are +2.0 and +1.3 kHz, respectively. The well-characterized space group and point symmetry in one of these compounds greatly simplifies the ^{31}P lineshape analysis, thus dispensing with the need to make assumptions about the interaction tensors involved. This offers a unique opportunity to study ΔJ by calculating dipolar coupling constants from known internuclear distances, and by using zero-field nuclear quadrupole resonance spectroscopy to obtain the magnitudes of the $^{63/65}\text{Cu}$ nuclear quadrupole coupling constants, C_Q . Copper-63 C_Q values in these complexes exceed 80 MHz, proving to be the largest reported for copper(I) phosphines. Phosphorus-31 NMR spectra of non-spinning samples at three applied magnetic fields are also presented, along with lineshape calculations based on full-matrix Zeeman-quadrupolar Hamiltonian diagonalization. It is shown that exact ^{31}P lineshape calculations provide the relative signs of C_Q , the isotropic J -coupling, and the effective dipolar coupling constant. This appears to be the first unambiguous determination of $\Delta^1J(^{31}\text{P}, ^{63/65}\text{Cu})$. © 1998 Academic Press

Key Words: copper(I) phosphines; anisotropic J tensor; lineshape calculations; $^{63/65}\text{Cu}$ NQR; solid-state ^{31}P NMR.

INTRODUCTION

A great many solid copper(I) phosphine complexes have been examined by ^{31}P cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy (1–5). Common to all such spectra are peak patterns distorted with respect to the symmetric quartet expected from pure J -coupling to a spin $3/2$ $^{63/65}\text{Cu}$ nucleus. The origin of this phenomenon has been thoroughly investigated and shown to arise from spin–spin coupling to a quadrupolar nucleus possessing a quadrupolar interaction which is not negligible relative to its Zeeman interaction (1b, 2, 6). Such spin–spin interactions are incompletely averaged under magic-angle spinning, and introduce field-dependent spectral distortions. The complete lineshape analysis in these cases can be complicated, relying as it does on the magnitudes and

relative orientation of the electric field gradient (EFG) and dipolar coupling tensors. In principle, this multivariate dependence offers information on the coupled quadrupolar nucleus not normally available from NMR studies of spin $1/2$ nuclei; practically, however, this complexity usually necessitates an estimate or assumption about the molecular structure or symmetry.

As a case in point, attempts have been made to identify anisotropy in $^1J(^{31}\text{P}, ^{63/65}\text{Cu})$ by analyses of ^{31}P NMR spectra (2). Lacking independent knowledge of the EFG at the copper nucleus and ^{31}P , $^{63/65}\text{Cu}$ dipolar coupling constants, some workers have assumed an axially symmetric EFG tensor which is coincident with the dipolar tensor. In still other cases, a *particular* value of ΔJ has been chosen and fixed, in order to obtain other parameters of interest (2b, 2d). While these assumptions may indeed be justified in certain cases, it is curious that no reports of $\Delta^1J(^{31}\text{P}, ^{63/65}\text{Cu})$ have appeared in which the local symmetry and structure are known to support the theoretical model. Herein, we report ^{31}P NMR spectra of spinning and non-spinning powder samples of two bis(tribenzylphosphine)cuprate(I) salts, $[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$ (1) and $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$ (2), which exhibit a two-coordinate, linear P–Cu–P geometry (7, 8). In 1, a three-fold rotation axis coincides with the P–Cu–P bond, thereby guaranteeing axial symmetry of the interaction tensors. By contrast, this rotational axis is lost in 2 due to minor distortions of the benzyl groups, leaving only the inversion centre at the copper nucleus. Perfect linearity is a rare structural occurrence in copper(I) phosphines (9); these systems generally experience competitive demands from the ligand donor strength and steric packing constraints in the determination of the resultant coordination number and space group symmetry. In combination with zero-field $^{63/65}\text{Cu}$ nuclear quadrupole resonance (NQR) data, exact lineshape calculations present a convincing demonstration of a substantial anisotropic component in the ^{31}P , $^{63/65}\text{Cu}$ J tensor.

BACKGROUND THEORY

Although the general theory relating to this work has been discussed (2c, 6d, 10), it is important to highlight some prop-

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erties of the various energy interactions pertinent to this investigation. Considering an isolated “spin pair” comprising the spin 1/2 nucleus (I) under NMR observation and a neighbouring quadrupolar nucleus (S), the total Hamiltonian operator can be written as the sum of the constituent Hamiltonians:

$$\mathcal{H} = \mathcal{H}_I^Z + \mathcal{H}_S^Z + \mathcal{H}_S^Q + \mathcal{H}_{IS}^D + \mathcal{H}_{IS}^J. \quad [1]$$

The first two terms, \mathcal{H}_I^Z and \mathcal{H}_S^Z , represent the combined shielding/Zeeaman Hamiltonian operators, accounting for the interaction of I and S with the applied magnetic field. The interaction of the quadrupolar nucleus with the electric field gradient (EFG) is represented by \mathcal{H}_S^Q . \mathcal{H}_{IS}^D and \mathcal{H}_{IS}^J are the direct dipolar and indirect spin–spin coupling interactions. The EFG is not, in general, axially symmetric, and its orientation in the molecular frame is unknown *a priori*. Likewise, the indirect spin–spin coupling interaction is generally non-axially symmetric, and its orientation is also unknown. The direct dipole–dipole coupling interaction, on the other hand, is axially symmetric, and (ignoring motional effects) is known to be situated with the unique component along the internuclear vector, r_{IS} . In general, therefore, the most rigorous analysis must consider two components for the (traceless) EFG tensor, three principal components for the \mathbf{J} tensor, and a dipolar coupling constant, as well as two sets of Euler angles describing the relative orientations of these three interactions. Clearly, the superposition of multiple spin interactions with general orientation-dependences can generate a convoluted scenario for the spectroscopist.

Given the complexity of this situation, it is no wonder that a few basic assumptions are often invoked to render the problem tractable. It is plausible, for example, that the \mathbf{J} tensor is axially symmetric, with its unique component directed along the internuclear vector. Under this condition, the tensors associated with \mathcal{H}_{IS}^D and \mathcal{H}_{IS}^J are coincident and can be described by three parameters: the direct dipole–dipole coupling constant, R_{DD} , and the isotropic and anisotropic contributions to the indirect spin–spin coupling tensor, J_{iso} and ΔJ . Further simplifications result from assumptions about \mathcal{H}_S^Q : if the EFG tensor is known to be both axially symmetric and along r_{IS} , then it is characterized by a single quadrupole coupling constant, $C_Q (=e^2qQ/h)$, the asymmetry parameter, η , being zero. Consequently, the original 10-variable problem reduces to a problem in four variables. Faced with a typical experimental scenario, it may be tempting to blindly introduce these assumptions in order to obtain at least something of interest from the spectral analysis, but it is important to expose the assumptions to which a model is subject, and to consider whether these are, in fact, valid. Fortunately, many practical circumstances are encountered in which symmetry arguments justify some of these simplifications.

The relative magnitudes of the interactions in Eq. [1] dictate the appropriate theoretical framework. The purely “high-field”

case arises where \mathcal{H}_S^Q is negligible with respect to \mathcal{H}_S^Z , measured in terms of the quadrupole frequency,

$$\nu_Q = \frac{3(e^2qQ/h)}{2S(2S-1)} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \quad [2]$$

and the Larmor frequency of the S nucleus, ν_S , respectively. The I spectrum under fast magic-angle spinning consists of $(2S + 1)$ peaks spaced equally by J_{iso} . As ν_Q increases, the quadrupolar nucleus is no longer solely quantized by the applied magnetic field, and the S eigenstates can be expressed as linear combinations of Zeeman states. For small values of ν_Q/ν_S , the influence of \mathcal{H}_S^Q can be treated as a perturbation to the Zeeman states, the spectral implications of which include peak spacings that differ from J_{iso} . This simple first-order approach has been amply discussed (6d) and exploited in many important cases. Beyond the limits of first-order perturbation theory, it becomes necessary to construct the full Zeeman-quadrupolar Hamiltonian and compute the eigenvalues numerically. This has been done recently for the case of samples spinning at the magic angle (1b, 2c, 10), but its application to stationary samples—though conceptually simpler—merits further comment.

The computational implementation developed herein is based on the theory presented by Menger and Veeman (1b), and can be described qualitatively in the following way. The quadrupole-perturbed Zeeman eigenstates can be expressed as linear combinations of the pure Zeeman states, the coefficients of which are obtained by diagonalization of the full S -spin Hamiltonian matrix:

$$\mathcal{H}_S = \mathcal{H}_S^Z + \mathcal{H}_S^Q. \quad [3]$$

Once the S -spin coefficients have been obtained for a given orientation of the magnetic field in the EFG principal axis system, the direct and indirect I - S dipolar interactions can be simply calculated as frequency shifts which add to the shielding. These frequencies are based on the expectation values of the spin angular momentum operators S_Z and S_X , which, in turn, are functions of the S -spin coefficients and the orientation of the magnetic field with respect to the dipolar vector. In this manner, the stationary powder spectrum can be computed by evaluating these terms for a sufficient number of orientations of the spin pair with respect to the applied magnetic field. The interested reader may refer to the cited literature for more detail (1b, 2c, 6a, 10).

RESULTS AND DISCUSSION

The ^{31}P CP/MAS spectra of compounds **1** and **2** obtained at 2.1, 4.7, and 9.4 T are presented, along with the best-fit calculations, in Fig. 1. The excellent agreement observed in these figures was achieved by employing full-matrix diagonal-

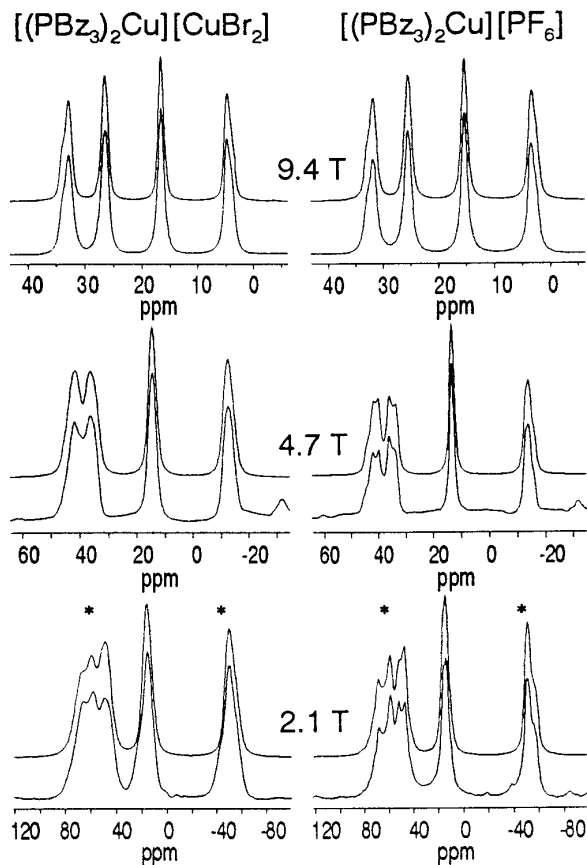


FIG. 1. Experimental (bottom traces) and calculated (top traces) ^{31}P CP/MAS spectra of the phosphine resonances in **1** and **2**; see Table 1 for fitting parameters. Each displayed spectral region spans 8 kHz. Rotation rates, 10000 Hz, 3000 Hz, and 3800 Hz for 9.4, 4.7, and 2.1 T, respectively. Number of transients: 1724, 138, 1428 for $[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$, and 2248, 60, 6740 for $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$, for 9.4, 4.7, and 2.1 T, respectively. Regions containing overlapping spinning sidebands are marked with asterisks (see Experimental).

ization of the $^{63/65}\text{Cu}$ Zeeman-quadrupolar Hamiltonian. Attempts to reproduce the experimental data using an approach based on first-order perturbation theory failed, implying that the magnitude of the quadrupole interaction is too large to be considered simply a perturbation on the Zeeman wavefunctions. Indeed, the strong field-dependence exhibited in Fig. 1 reflects the importance of the relative magnitudes of the Zeeman and quadrupolar interaction in determining spectral appearance. The ratio, $\nu_Q(^{65}\text{Cu})/\nu_S(^{65}\text{Cu})$, for example, ranges from 0.4 to 1.8 on going from 9.4 T to 2.1 T, with the associated lineshapes becoming correspondingly more distorted from the purely “high-field” case of a quartet with equal splittings of $^1J(^{31}\text{P}, ^{65}\text{Cu})$.

Spin 1/2 lineshape calculations involving coupled quadrupolar nuclei are influenced by the magnitude of the electric field gradient (EFG) tensor and its orientation with respect to the dipolar tensor. In the most general case, this necessitates knowledge of the nuclear quadrupole coupling constant, C_Q , the EFG asymmetry parameter, η , and the angles, α and β ,

orienting the dipolar vector in the EFG principal axis system (2c). Clearly, this information can be hard to obtain, and in many applications, assumptions are invoked to make lineshape calculations possible (*vide supra*). The attractiveness of compound **1** is that single-crystal X-ray diffraction results indicate a perfectly linear P–Cu–P centre, located on a three-fold rotation axis with an accompanying inversion centre at the copper nucleus (7). This symmetry arrangement requires that the copper EFG tensor be axially symmetric, with the largest component directed along the P–Cu bond. Since the dipolar vector is always understood to be collinear with the internuclear axis, the dipolar and EFG tensors are coincident. In terms of the aforementioned parameters, the space group symmetry in this system ensures that $\eta = 0$, and the Euler angles α and β are zero. In addition, this symmetry guarantees that the \mathbf{J} tensor is axially symmetric with the unique axis being along $r_{\text{P,Cu}}$ (11). As such, many of the assumptions commonly made to render lineshape calculations tractable are justified in this case.

Moreover, axial symmetry in the EFG tensor justifies the use of NQR spectroscopy to determine independently the quadrupole coupling constants. For a spin 3/2 nucleus subject to an axially symmetric EFG, $|C_Q|$ is simply twice the measured quadrupole frequency, ν_Q (see Eq. [2]). These values, given in Table 1, are 84.6 and 78.3 MHz for the ^{63}Cu and ^{65}Cu isotopes of **1**. These couplings appear to be the largest reported for copper(I) phosphine complexes (12), and their magnitudes are reflected in the marked field-dependence demonstrated by the ^{31}P CP/MAS spectra of Fig. 1. On the basis of the X-ray diffraction and NQR data, all the relevant information regarding the $^{63/65}\text{Cu}$ EFG tensors, except for the sign of C_Q , is

TABLE 1
NMR and NQR Data for bis(tribenzylphosphine)cuprates, 1 and 2

	$[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$	$[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$
$\delta_{\perp}^{a,b}$	+40.6 (2)	+38.4 (2)
$\delta_{\parallel}^{a,b}$	−21.2 (2)	−20.6 (2)
$\delta_{\text{iso}}^{a,c}$	+19.8 (2)	+18.9 (2)
$R_{\text{DD}}(^{31}\text{P}, ^{63}\text{Cu})^{d,e}$	+1223	+1230
$^1J_{\text{iso}}(^{31}\text{P}, ^{63}\text{Cu})^{d,f}$	+1535 (10)	+1550 (10)
$^1J_{\parallel}(^{31}\text{P}, ^{63}\text{Cu})^{d,f}$	+2035 (50)	+2030 (50)
$^1J_{\perp}(^{31}\text{P}, ^{63}\text{Cu})^{d,f}$	+1285 (50)	+1310 (50)
$C_Q(^{63}\text{Cu})^g$	+84.60 (57.06) ^h	+82.96
$C_Q(^{65}\text{Cu})^g$	+78.30 (52.80) ^h	+76.76

^a ^{31}P chemical shifts, in ppm, relative to external 85% $\text{H}_3\text{PO}_4(\text{aq})$.

^b Obtained from ^{31}P CP NMR of stationary powder samples.

^c Obtained from ^{31}P CP/MAS.

^d Parameters for ^{31}P , ^{65}Cu spin pairs were varied according to their relative magnetogyric ratios, e.g., $^1J(^{31}\text{P}, ^{65}\text{Cu})/^1J(^{31}\text{P}, ^{63}\text{Cu}) = 1.071$.

^e Dipolar coupling constants, in Hz, calculated from known values of $r_{\text{P,Cu}}$.

^f Spin–spin coupling parameters, in Hz, determined from ^{31}P CP/MAS.

^g Nuclear quadrupole coupling constants, in MHz; magnitudes obtained from NQR.

^h Nuclear quadrupole coupling constants, in MHz, obtained from NQR for the linear $[\text{Br-Cu-Br}]^-$ anion.

provided at the outset, thereby eliminating the need for approximations.

Since X-ray crystallography also provides bond lengths, the P–Cu dipolar coupling constant, R_{DD} , can be calculated according to (13)

$$R_{\text{DD}}(^{31}\text{P}, ^{63}\text{Cu}) = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{2\pi}\right)\gamma(^{31}\text{P})\gamma(^{63}\text{Cu})\langle r_{\text{P,Cu}}^{-3}\rangle, \quad [4]$$

where $\langle r_{\text{P,Cu}}^{-3}\rangle$ represents a time average over the internuclear distance, cubed. This leaves only the isotropic ^{31}P chemical shift and the \mathbf{J} tensor as variable parameters in the fitting procedure. The indirect spin–spin coupling tensor is commonly separated into an isotropic J -coupling constant, and an orientation-dependent anisotropic component representing the difference between the parallel and perpendicular components of an axially symmetric tensor, $\Delta J = J_{\parallel} - J_{\perp}$ (13, 14). Due to this orientation-dependence being identical to that of the *direct* dipolar interaction, an *effective* dipolar coupling constant is usually defined which incorporates the effects of this anisotropy: $R_{\text{eff}} = R_{\text{DD}} - \Delta J/3$. In practice, it is impossible to separate these two contributions, with the consequence that the dipolar coupling constant measured in solid-state NMR experiments is always R_{eff} . This can be used to advantage if one is interested in determining ΔJ , as in the present case: since R_{DD} is known independently, the difference between R_{eff} and R_{DD} yields $\Delta J/3$.

In the NMR spectral analysis of **1**, the ^{31}P CP/MAS line-shapes could not be reproduced without introducing a sizeable, positive ΔJ . Figure 2 depicts simulated spectra at 4.7 T with no \mathbf{J} anisotropy, and with positive and negative values of ΔJ . By comparison with Fig. 1, it is clear that only the spectrum calculated using $\Delta^1 J(^{31}\text{P}, ^{63}\text{Cu}) = +750$ Hz agrees with the experimental spectrum.² That the same parameters accurately fit ^{31}P CP/MAS spectra at three applied fields serves to corroborate this conclusion (see Table 1). Under the conditions of first-order perturbation theory, multiple field data may only make the phenomenon more or less apparent, but offer no *new* information since the parameters are linearly correlated with the applied field strength. On the other hand, where the quadrupole and Zeeman interactions are of comparable magnitude and the full-matrix diagonalization method is used, analyses of NMR spectra collected at different fields enhance confidence in the NMR parameters obtained therefrom.

Information regarding the anisotropic ^{31}P chemical shielding is available from cross-polarization spectra of non-spinning samples (Fig. 3). Again utilizing the symmetry constraints provided by X-ray diffraction to guarantee an axially symmetric shielding tensor in **1**, exact lineshape calculations yield the

² All simulated spectra include coupling effects to both spin-active copper nuclei according to the ratio of their respective natural abundance, $^{63}\text{Cu}/^{65}\text{Cu} = 69.1/30.9$. Dipolar and J -couplings were varied according to their relative magnetogyric ratios, $\gamma(^{63}\text{Cu})/\gamma(^{65}\text{Cu}) = 0.93353$.

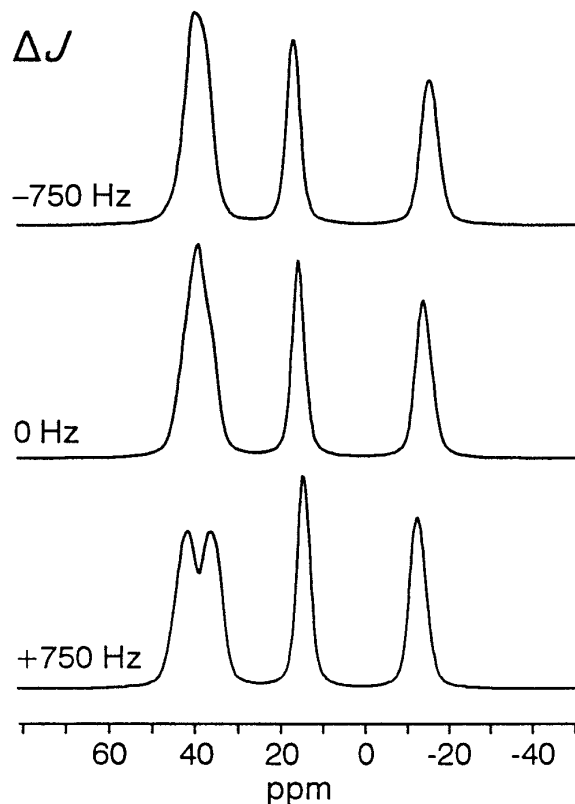


FIG. 2. Sensitivity of ^{31}P MAS calculations to the sign and magnitude of $\Delta^1 J(^{31}\text{P}, ^{63/65}\text{Cu})$ for **1** at 4.7 T. Other simulation parameters can be found in Table 1.

following components: $\delta_{\perp} = +40.6$ ppm and $\delta_{\parallel} = -21.2$ ppm (Table 1). Shielding anisotropy is indicated by the span of the tensor, $\Omega = \delta_{\perp} - \delta_{\parallel} = 62$ ppm, with the largest shielding effects observed when the P–Cu–P core is aligned with the applied magnetic field. Although ^{31}P shielding anisotropies have been determined for many transition metal phosphine complexes, there are very few examples involving group 11 metals (15). In fact, this appears to be the first report of ^{31}P chemical shift tensor components in a copper(I) phosphine complex. Qualitatively, the span of the chemical shielding tensor in **1** is significantly smaller than those generally observed in phosphine complexes of transition metals from groups 6 to 10 (16), but is comparable to those of mercury phosphine complexes (17) and free phosphine ligands (18).

A second bis(tribenzylphosphine)cuprate, $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$, (**2**) was also investigated by these means. The crystal belongs to the space group $C2/c$ (8). This symmetry guarantees that the copper in any given cation is situated on a centre of inversion, consequently ensuring that the P–Cu–P bond angle is 180° , and that the two phosphorus nuclei are magnetically equivalent. However, the crystal symmetry *does not* demand that the EFG tensor at the Cu(I) site is axially symmetric, nor does it dictate that the unique components of the direct and indirect spin–spin coupling tensors be coincident (11). A further implication of

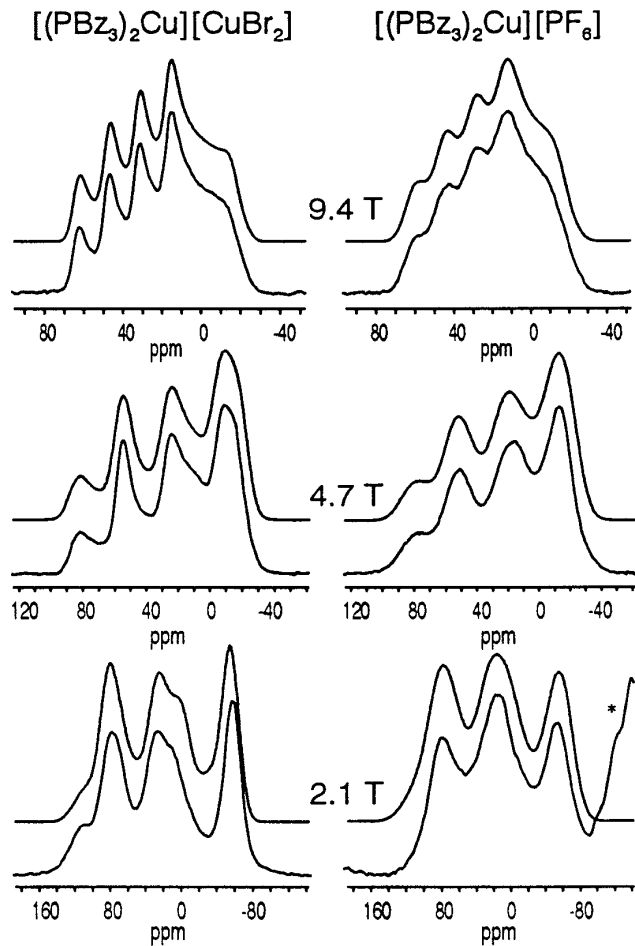


FIG. 3. Experimental (bottom traces) and calculated (top traces) ^{31}P CP spectra of the phosphine resonances in stationary samples of **1** and **2**; see Table 1 for fitting parameters. Spectra collected at 9.4 and 4.7 T result from between 200 and 300 transients, whereas 2.1 T spectra are from the coaddition of 11,400 transients. A portion of the hexafluorophosphate resonance in the 2.1 T spectrum of $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$ is indicated by an asterisk.

the lowered symmetry is that the ^{31}P NMR analysis of non-spinning samples cannot rely on the assumption that the phosphorus shielding tensors are exactly axially symmetric. The local environment about the phosphorus is distorted somewhat from the perfect three-fold rotational symmetry of **1**; the Cu–P–C bond angles are 110.5° , 114.0° , and 115.6° (8).

In spite of these qualifications, excellent simulations of the ^{31}P NMR spectra of magic-angle spinning and non-spinning samples of **2** could be obtained by invoking the above assumptions (Figs. 1 and 3). Moreover, the spectral parameters are within experimental error of those obtained for **1** (Table 1). Nevertheless, without having carefully examined compound **1**, for which symmetry-dictated tensor orientations can be relied upon, it would be impossible to have any confidence in the $\mathbf{J}(^{31}\text{P}, ^{63/65}\text{Cu})$ anisotropy obtained for **2**. A clear message emerging from this work is that the reliable characterization of

anisotropic \mathbf{J} tensors in powder samples depends critically on sufficiently high crystal symmetry.

An unique feature of these spectral analyses is that relative sign information is available from the exact calculations. Given that one-bond reduced coupling constants (19) between ^{31}P and transition metals are known to be positive (14), only positive values of C_Q and R_{eff} reproduce the experimental spectra. A positive nuclear quadrupole coupling constant is consistent with sign predictions for linear “*sp*-hybridized” atoms based on symmetry and hybridization considerations (2b, 20), as well as with microwave spectroscopic measurements in copper(I) halides (21, 22). Since the magnetogyric ratios, $\gamma(^{31}\text{P})$ and $\gamma(^{63/65}\text{Cu})$, possess the same sign, R_{DD} must also be positive. A positive value of R_{eff} then, demands that $\Delta J/3$ be smaller than R_{DD} , a criterion satisfied by the values listed in Table 1. In fact, two sets of parameters produce identical spectra, the second involving the corresponding *negative* quantities for C_Q , J_{iso} , and R_{eff} . Were this latter solution valid, the \mathbf{J} anisotropy would have to be $+6588$ Hz in **1** to yield $R_{\text{eff}} = -973$ Hz!

It is worth emphasizing that what emerge from this type of analysis are the *relative* signs of C_Q , J_{iso} , and R_{eff} (2c, 23). Unless one of these is known *a priori*, it is not possible to distinguish absolutely between these two solutions. Early calculations by Menger and Veeman claiming to have determined the *absolute* sign of $^1J(^{31}\text{P}, ^{63}\text{Cu})$ were based on purely isotropic J -coupling (i.e., $R_{\text{eff}} = R_{\text{DD}} > 0$), thereby inadvertently overlooking the possibility of a *negative* effective dipolar coupling constant (1b). Subsequent workers have elected instead to assume the sign of C_Q in order to determine the sign of J_{iso} (2c). An alternate approach, as employed here, is to accept the positive sign of the reduced coupling constant, $^1K(\text{P}, \text{Cu})$ (19), as a reference for the other signs. Although the end result is the same in this case, it is important to have a clear understanding of what is actually *known* in order to avoid circular reasoning.

If internuclear distances were not known independently, one might be tempted to use the effective dipolar coupling constant in the calculation of $r_{\text{P,Cu}}$, i.e., assuming purely isotropic J -coupling. In the present cases, this would result in an overestimation of the bond length. Specifically, the actual phosphorus-copper bond length in $[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$ is $2.1955(14)$ Å, yielding $R_{\text{DD}}(^{31}\text{P}, ^{63}\text{Cu}) = +1223$ Hz (7). Accounting for $\Delta^1J(^{31}\text{P}, ^{63}\text{Cu}) = +750(50)$ Hz, the effective dipolar coupling constant is 972 Hz, leading to an *apparent* $r_{\text{P,Cu}}$ of 2.37 Å. Similarly for $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$, $r_{\text{P,Cu}} = 2.1909(14)$ Å from crystallography (8), whereas the NMR result neglecting the contribution of ΔJ is 2.36 Å. In each case, a naive interpretation of the solid-state NMR spectra would indicate bond lengths 8% *longer* than those determined from X-ray crystallography. Clearly, this observation underscores the importance of considering whether anisotropic J -coupling may be operative in the analysis and subsequent interpretation of solid-state NMR spectra (24).

It is necessary to point out that the comparison of bond lengths obtained from solid-state NMR and diffraction tech-

niques is subject to some qualifications. In particular, the measurement of dipolar couplings depends on the vibrationally averaged value $\langle r^{-3} \rangle$, so that the internuclear distances derived therefrom are actually $(\langle r^{-3} \rangle)^{-1/3}$. Diffraction techniques, by contrast, measure the time average $\langle r \rangle$. It is well known, therefore, that molecular libration decreases the observed dipole coupling constant, thereby *increasing* the apparent bond length (25). Could motional averaging masquerade as indirect spin–spin coupling anisotropy? Recent research utilizing theoretical calculations and molecular dynamics simulations to assess vibrational effects on internuclear distances obtained from solid-state NMR concluded that for directly bonded non-proton nuclei in glycine, molecular librations are responsible for a 2–3% increase in bond lengths with respect to those obtained from single crystal diffraction techniques (25*c*). The same study suggests that intramolecular vibrations induce negligible changes between nonproton nuclei. On the basis of these results, it is highly unlikely that motional effects are fully responsible for the observed 8% increase in the P–Cu bond length; ΔJ must be operative.

The existence of anisotropic *J*-coupling in metal phosphines has been thoroughly discussed in the literature (2, 17, 23, 26, 27), and is understood to imply that mechanisms other than the orientation-*independent* Fermi contact term play a significant role in indirect spin–spin coupling. In view of this, it is not surprising that schemes correlating $^1J(^{31}\text{P}, ^{63}\text{Cu})$ with the number of bound phosphine ligands (28) fail in the present case, as they are implicitly based on the dominance of the Fermi contact mechanism. Whereas this assumption appears to be valid for first-row elements such as ^{13}C and ^1H , its extension to heavier elements is dubious given the results contained herein.

CONCLUSIONS

The analysis of ^{31}P NMR spectra of compound **1** is simplified by the space group symmetry which, when combined with single-crystal X-ray diffraction and powder NQR data, permits an unambiguous measurement of $\Delta^1J(^{31}\text{P}, ^{63/65}\text{Cu})$. The corresponding analysis of **2**, subject to the same assumptions, yields NMR parameters that are within experimental error of **1**, in spite of the loss of strict three-fold symmetry. The spectral calculation of **2** can be considered successful only because it is accompanied by the parallel success of **1**, for which the interaction tensors are completely determined by crystal symmetry. Though sometimes ignored, the contribution of ΔJ to the effective dipolar coupling constant can be substantial, and its neglect may yield misleading structural information. These results are in qualitative agreement with conclusions from previous studies which were based on questionable assumptions (2). Clearly it is of paramount importance to establish simple methods for understanding NMR spectra in terms of molecular structure, but it is difficult to overemphasize the need to maintain scientific rigour in the presentation of such

schemes. In particular, the potential utility of solid-state NMR in structural characterization is not ultimately aided by “quick-and-dirty” spectral analyses which account insufficiently for the tensorial complexity of nuclear coupling interactions, but will be furthered only by detailed investigations of well-characterized molecular systems.

EXPERIMENTAL

Sample preparation and characterization. $[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$, **1**, (Bz \equiv benzyl) was prepared according to the literature method of Akrivos *et al.* (7). The synthesis of $[(\text{PBz}_3)_2\text{Cu}][\text{PF}_6]$, **2**, fully described in Ref. (8), involved the addition of solid tribenzylphosphine to a solution of $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ in dichloromethane/ethanol (1:1) under nitrogen atmosphere. This reaction mixture was heated under reflux for five minutes and allowed to stand at room temperature for one hour, whereupon colourless crystals of **2** were filtered, washed with ice-cold ethanol and dried *in vacuo*. The single-crystal X-ray structures of **1** (7) and **2** (8) confirm that these complexes possess discrete $[(\text{PBz}_3)_2\text{Cu}]^+$ cations with linear, two-coordinate P–Cu–P local environments for the Cu(I) atom. In both complexes, the copper atom of the cation is located on a centre of symmetry such that the P–Cu–P angle is exactly 180° and the two ligands are perfectly staggered and of opposite chirality. In **1**, the P–Cu–P axis lies on a three-fold crystallographic symmetry axis, generating C_3 symmetry for the ligands and S_6 symmetry for the cation; the entire system crystallizes in the $R\bar{3}$ space group (7). In **2**, the three-fold symmetry axis along P–Cu–P is perturbed, as the F(3) and F(3') atoms of the $[\text{PF}_6]^-$ anion interact with the *ortho* hydrogens of one phenyl group on each of the PBz_3 ligands; this system crystallizes in the $C2/c$ space group (8).

$^{63/65}\text{Cu}$ nuclear quadrupole resonance spectroscopy. ^{63}Cu and ^{65}Cu quadrupole frequencies were obtained at ambient temperature using a Bruker CXP console pulsing into a probe arrangement that was well-removed from the magnet (>5 m) and shielded from extraneous magnetic and radiofrequency interference by a mumetal container. Solid-echo experiments with extended phase cycles (29) to eliminate baseline distortions and echo tails were employed in these measurements, using hard pulses of 2- μs duration and recycle delays of 0.5 s. The quadrupole frequency range scanned was determined from previous NQR studies of Cu(I) systems (12). The location of both ^{63}Cu and ^{65}Cu isotope resonances (related by the ratio $\nu_Q(^{63}\text{Cu})/\nu_Q(^{65}\text{Cu}) = 1.081$) verified that true copper NQR frequencies were being observed. For $[(\text{PBz}_3)_2\text{Cu}][\text{CuBr}_2]$, the NQR frequencies for the $[\text{CuBr}_2]^-$ anion were measured and proved to be well-separated from the cationic P–Cu–P core of interest. The values reported for $[\text{CuBr}_2]^-$ are in close agreement with previous $^{63/65}\text{Cu}$ NQR studies involving this anion (12*c*).

^{31}P nuclear magnetic resonance spectroscopy. ^{31}P CP/MAS spectra were acquired at three fields using Bruker CXP-

90, MSL-200, MSL-400, and AMX-400 spectrometers operating at 36.44, 81.03, and 161.98 MHz, respectively. Samples were packed into 4 mm or 7 mm zirconia rotors and all spectra were collected at 298 K. Chemical shifts are reported relative to 85% $\text{H}_3\text{PO}_4(\text{aq})$. Standard cross-polarization schemes were used, typically employing proton 90° pulses of 3.5 μs and contact times of 10 ms, with 60 s recycle delays. For MAS spectra, data tables of 2K points were acquired and zero-filled to 4K prior to exponential multiplication with 30 Hz Lorentzian line-broadening and Fourier transformation. Spectra of stationary samples typically involved the acquisition of 1K points, $2\times$ zero-filling, and exponential multiplication of 100 Hz, prior to Fourier transformation. The spectral width ranged from 50 to 80 kHz.

In order to establish meaningful comparisons between experimental and calculated MAS lineshapes, it is necessary to construct an "isotropic MAS powder spectrum" by adding the spinning sidebands (ssbs) to the centreband (30). For spectra collected at 9.4 T, this was achieved by summing the minor intensity (<5%) located in the ± 1 order ssbs, well-separated from the centreband. At 4.7 T, however, the rotation rate was insufficient to fully separate the ssbs from the centreband, and consequently, intensity from first-order ssbs was interleaved between centreband peaks. Summation of the ± 1 and ± 2 ssbs in this case therefore, yielded peak artifacts which, though unsightly, do not interfere with the spectral analysis; these have been artificially removed for aesthetic purposes. In MAS spectra acquired at 2.1 T, spinning sidebands overlap with peaks from the centreband, and it was impossible to generate an "isotropic MAS powder spectrum." Although these constitute a small percentage of the total signal intensity (<10%), this spectral overlap is probably responsible for minor discrepancies observed between calculated and experimental spectra at this field (see Fig. 1).

NMR spectral calculations. Calculations of the ^{31}P NMR lineshapes utilized WSolids and QUADSPIN, both C programs developed in this laboratory incorporating full-matrix diagonalization of the Zeeman-quadrupolar Hamiltonian for the dipolar-coupled quadrupolar nucleus (10). For calculating spectra of stationary powder samples, the formal A_2X spin system was treated as an AX system, since incorporation of the small ^{31}P , ^{31}P dipolar coupling constant (230 Hz) simply introduced additional broadening of the peaks. Powder averaging was performed using the POWDER algorithm (31).

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