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Structural, Far-IR, and Solid State ^{31}P NMR Studies of Two-Coordinate Complexes of Tris(2,4,6-trimethoxyphenyl)phosphine with Copper(I) Iodide

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Reaction of the highly basic, sterically hindered tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) with copper(I) iodide in acetonitrile yields 1:1 complexes whose structures depend on the mole ratio of the reactants. The crystals which first deposit from the reaction of TMPP with CuI in a 1:2 ratio are the 1:1 molecular adduct [(TMPP)CuI], whose structure was determined by room-temperature single-crystal X-ray studies. This complex is isomorphous with the corresponding Cl and Br compounds and their Ag analogues, crystallizing in the tetragonal space group $P4_3$, with a = 15.292(7) Å, c = 12.748(5) Å, Z = 4, and R = 0.044 for N_o = 2027 "observed" ($I > 3\sigma(I)$) reflections. The complex contains mononuclear [(TMPP)CuI] molecules with approximately linear two-coordination about the copper atom; Cu–P = 2.188(4) Å, Cu–I = 2.417(2) Å, P–Cu–I = 171.0(1)°. The slight deviation from linearity presumably arises because of contacts with the methoxy oxygen atoms; the Cu---O contacts involving the nearest *ortho*-methoxy oxygen atoms on the three phenyl groups in the ligand are 3.07(1), 2.858(7), and 2.674(9) Å. This represents the first structural characterization of a compound with a two-coordinate P–Cu–I grouping, and the first example of a two-coordinate complex of CuI with a neutral ligand. The far-infrared spectrum shows a ν(Cu–I) band at 239 cm^{-1}. Reaction of TMPP with CuI in a 1:1 mole ratio in acetonitrile yields a different product of 1:1 stoichiometry which is shown by means of solid state ^{31}P NMR and IR spectroscopy to be an ionic complex of the type [(TMPP)$_2$Cu]$_n$[Cu$_n$I$_{2n}$].

Introduction

There is a considerable variation in coordination behavior between the different members of the group 11, or coinage metals, in their monovalent (d^{10} configuration) state. Thus, for Au^{I}, linear two-coordination is by far the most common situation, whereas for Cu^{I} and Ag^{I}, tetrahedral four-coordination is more frequently encountered. The early postulation of species such [Ag(NH$_3$)$_2$]$^+$ and [MX$_2$]$^-$ (M = Cu, Ag; X = Cl, Br, I) suggested that two-coordination would be common for Cu^{I} and Ag^{I}, but subsequent studies have shown that this is not the case and that this type of coordination is rather rare among their inorganic complexes.[2–4] Two-coordination has been found, for example, in complexes with anionic ligands such as halide[4–8] and cyanide[9] and with neutral ligands such as NH$_3$[10] and amines.[11,12] With these ligands, the factors that determine the low coordination number appear to be electronic, although in some cases steric factors may also be important.[11] By contrast, complexes of Cu^{I} and Ag^{I} with tertiary phosphine ligands generally display a coordination number of 4,[2,3,13–17] although examples of three-coordination have been observed with the ligand triphenylphosphine, PPh$_3$.[18–20] Two-coordination can only be achieved by using more sterically demanding ligands.[21–24]

Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) is both a very basic and a sterically very hindered phosphine ligand,[25,26] and a number of coordination complexes of this ligand that have unusual coordination geometries were recently reported.[23,24,27–29] We previously showed that this ligand forms mononuclear adducts [(TMPP)MX] (M = Cu, Ag; X = Cl, Br) which contain almost linear two-coordinate copper(I) or silver(I), a slight deviation from linearity (P–M–X angles in the range 173–175°) being associated with a weak interaction with one of the *ortho*-methoxy

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Table 1. Summary of Crystal Data for [(TMPP)CuI]

formula	$C_{27}H_{33}CuIO_9P$	Z	4
fw	722.7	D_c/g cm^{-3}	1.61
cryst syst	tetragonal	μ_{Mo}/cm^{-1}	18.7
space group	$P4_3$ (C_4^4, No. 78)	$A^*_{\rm min,max}$	1.42, 1.58
T/K	295	$2\theta_{\rm max}$/deg	60
λ/Å	0.7107_3	N, N_o	3656, 2027
a/Å	15.292(7)	R^a	0.044
c/Å	12.748(5)	$R_w{}^b$	0.043
V/Å^3	2981		

^{a} $R = (\sum\Delta|F|)/(\sum|F_o|)$. ^{b} $R_w = ((\sum w\Delta|F|^2)/(\sum w|F_o|^2))^{1/2}$.

Table 2. Non-Hydrogen Atom Coordinates for [(TMPP)CuI]

atom	x	y	z
Cu	0.64523(9)	0.77842(9)	1.00000
I	0.50632(5)	0.80097(6)	1.0864(1)
P	0.7587(2)	0.7531(2)	0.8999(3)
C(11)	0.7893(6)	0.8472(6)	0.818(1)
C(12)	0.7228(7)	0.8888(8)	0.767(1)
O(12)	0.6431(5)	0.8476(5)	0.7736(8)
C(121)	0.568(1)	0.889(1)	0.733(2)
C(13)	0.7357(9)	0.9623(8)	0.709(1)
C(14)	0.8167(9)	1.0003(7)	0.706(1)
O(14)	0.8248(7)	1.0751(6)	0.6476(8)
C(141)	0.907(1)	1.119(1)	0.652(2)
C(15)	0.8879(8)	0.9594(7)	0.755(1)
C(16)	0.8737(8)	0.8836(7)	0.812(1)
O(16)	0.9396(5)	0.8470(5)	0.8686(7)
C(161)	1.0229(8)	0.854(1)	0.833(2)
C(21)	0.7288(7)	0.6585(7)	0.820(1)
C(22)	0.6931(7)	0.5873(7)	0.874(1)
O(22)	0.6916(5)	0.5981(5)	0.9799(7)
C(221)	0.653(1)	0.5329(9)	1.040(1)
C(23)	0.6633(7)	0.5143(7)	0.825(1)
C(24)	0.6671(7)	0.5119(7)	0.716(1)
O(24)	0.6333(6)	0.4359(6)	0.6732(8)
C(241)	0.622(1)	0.4319(9)	0.562(1)
C(25)	0.7008(7)	0.5778(8)	0.657(1)
C(26)	0.7331(7)	0.6511(8)	0.712(1)
O(26)	0.7691(6)	0.7198(5)	0.6570(7)
C(261)	0.771(1)	0.720(1)	0.548(1)
C(31)	0.8510(7)	0.7163(7)	0.973(1)
C(32)	0.8532(8)	0.7221(7)	1.083(1)
O(32)	0.7840(6)	0.7644(6)	1.1267(7)
C(321)	0.763(1)	0.748(1)	1.227(2)
C(33)	0.923(1)	0.689(1)	1.141(1)
C(34)	0.9868(9)	0.6494(9)	1.093(2)
O(34)	1.0536(8)	0.6206(8)	1.170(1)
C(341)	1.111(1)	0.577(2)	1.126(2)
C(35)	0.9920(8)	0.6384(8)	0.986(2)
C(36)	0.9218(8)	0.6709(8)	0.923(1)
O(36)	0.9167(5)	0.6652(6)	0.8194(8)
C(361)	0.980(1)	0.625(1)	0.762(1)

oxygens in the ligand.[23,24] There are indications, however, that the situation for the corresponding X = I complexes is somewhat different from that of the other halides. Thus, while ^{31}P NMR studies suggested the existence of [(TMPP)AgI] in solutions of the product of the 1:1 reaction of TMPP and AgI, the IR and ^{31}P CP MAS NMR spectra of the solid product showed that this contains the complex cation $[(TMPP)_2Ag]^+$.[24] This was confirmed by an X-ray structure determination.[28] The aim of the present study was to investigate the reaction between TMPP and CuI or AgI more thoroughly, with a view to obtaining the mononuclear two-coordinate [(TMPP)MI] complexes, as no such complexes of CuI or AgI with neutral ligands have yet been reported.

Experimental Section

Preparation of Compounds. The ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) was prepared according to the procedure outlined in the literature[25] by the reaction of $P(OPh)_3$ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization of the solid product from ethanol.

Synthesis of Iodo(tris(2,4,6-trimethoxyphenyl)phosphine)copper(I), [(TMPP)CuI]. Tris(2,4,6-trimethoxyphenyl)phosphine (0.0887 g, 0.167 mmol) and CuI (0.0639 g, 0.336 mmol) were placed in a small Schlenk tube under nitrogen. Degassed acetonitrile was added and the mixture heated with stirring in a hot water bath. Complete dissolution of the solids occurred after a few minutes. On cooling of the solution, small colorless crystals of product formed. These were collected by vacuum filtration and dried *in vacuo*. Mp: 193 °C dec. Anal. Calcd for [(TMPP)CuI] ($C_{27}H_{33}CuIO_9P$): C, 44.9; H, 4.6. Found: C, 44.8; H, 4.6. Upon standing for several days under nitrogen, the filtrate deposited a white solid whose far-IR spectrum was different from that of the crystals which first deposited from the reaction solution. The attempted synthesis of the 1:1 adduct in a reaction analogous to that which yields the corresponding chloro and bromo complexes, using a 1:1 mole ratio of the reactants,[23] gave a white microcrystalline powder that gave approximately correct analysis data for a 1:1 TMPP:CuI complex (found: C, 44.5; H, 4.5) but which, on the basis of the ensuing spectroscopic studies, was found to have a structure that is more complex than that of the simple 1:1 neutral adduct described above (see Results and Discussion).

Synthesis of Bis(tris(2,4,6-trimethoxyphenyl)phosphine)copper(I) Perchlorate, $[(TMPP)_2Cu][ClO_4]$. This complex was prepared by a literature method.[25] Anal. Calcd for $[(TMPP)_2Cu][ClO_4]$ ($C_{54}H_{66}ClCuO_{22}P_2$): C, 52.8; H, 5.4. Found: C, 52.5; H, 5.7.

Synthesis of Chloro- and Bromo(tris(2,4,6-trimethoxyphenyl)phosphine)copper(I), [(TMPP)CuX] (X = Cl, Br). These were prepared by a previously described method.[23]

X-ray Crystal Structure Determination. Crystal and refinement data for [(TMPP)CuI] are given in Table 1. A unique data set was measured at ≈295 K using a specimen mounted in a capillary, within the limit $2\theta_{\rm max}$ = 60° (ENRAF-Nonius CAD-4 diffractometer, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; $2\theta/\theta$ scan mode) yielding 3656 independent reflections, 2027 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\rm iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$ at convergence R, R_w are 0.044, 0.043, the statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\rm diff}) + 0.0004\sigma^4(I_{\rm diff})$ being used. Neutral-atom complex scattering factors were employed, computation using the XTAL 3.0 program system implemented by Hall.[30] Final atom coordinates are given in Table 2, and the structure is shown in Figure 1. Atom labeling and setting (as $P4_1$ or, as here, its enantiomer $P4_3$) are in conformity with those established previously for the chloride and the bromide.[23]

Spectroscopy. Far-infrared spectra were recorded at 4-cm^{-1} resolution at room temperature as pressed polythene disks on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 6.25-μm Mylar film beam splitter, a mercury lamp source, and a TGS detector. Solid state cross-polarization magic-angle-spinning (CP/MAS) $^{31}P\{^1H\}$ NMR spectra were obtained at ambient temperature on a Varian Unity 400 spectrometer at 161.92 MHz. Single contact times of 1 ms were used with a proton pulse width of 7.8 μs, a proton decoupling field of 52 kHz, and a recycle delay time of 30 s. The samples were packed in Kel-F inserts within silicon nitride rotors and spun at a speed of 5 kHz at the magic angle. Between 60 and 200 FID's were collected and transformed with an experimental line broadening of 50 Hz. Chemical shift data are referenced to 85% H_3PO_4 via an external sample of solid PPh_3 (δ = −9.9 ppm).

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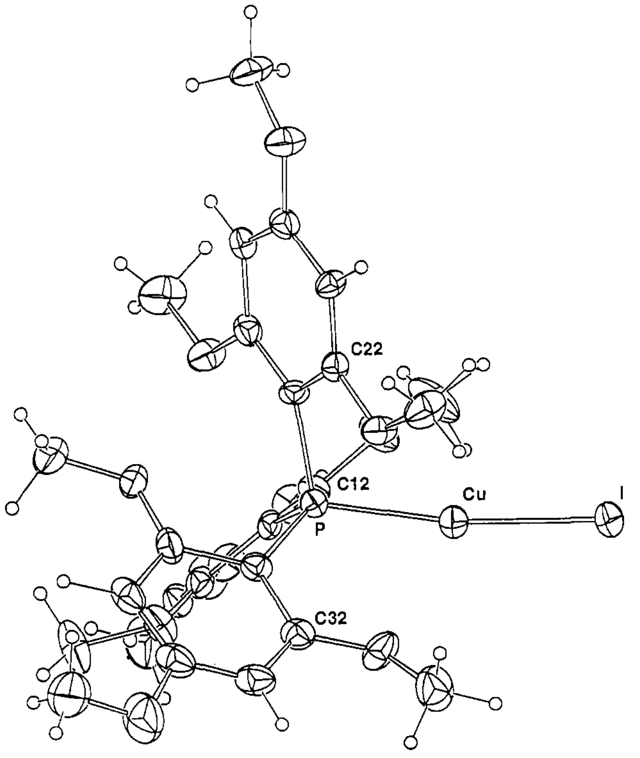

Figure 1. Structure of [(TMPP)CuI]. The 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å.

Results and Discussion

Syntheses. The reaction of TMPP with CuX (X = Cl, Br) in a 1:1 mole ratio in acetonitrile yielded 1:1 adducts which were previously shown by single-crystal X-ray studies to contain molecular [(TMPP)CuX] species involving two-coordinate copper(I).[23] The corresponding reaction for X = I yielded a solid product from which suitable crystals for a structure determination could not be obtained. Unlike the chloro and bromo complexes, which showed strong ν(CuX) bands in the far-IR,[23] the iodo complex showed no such band. Similar results were subsequently obtained for the corresponding AgX complexes, and it was shown that the product from the AgI reaction is probably a mixture of various compounds containing the $[(TMPP)_2Ag]^+$ complex.[24,28] This suggests that there is a complex set of equilibria in solution:

$$\mathrm{MX + L \rightleftarrows [LMX]} \qquad (1)$$

$$\mathrm{[LMX] + L \rightleftarrows [L_2M]^+ + X^-} \qquad (2)$$

$$\mathrm{X^- + MX \rightleftarrows [MX_2]^-} \qquad (3)$$

$$\mathrm{[MX_2]^- + MX \rightleftarrows [M_2X_3]^-} \qquad (4)$$

etc.

The formation of $[L_2M]^+$ is favored by the presence of excess ligand (eq 2), so solutions with a greater than 1:1 ligand:MX ratio should be avoided if it is desired to produce the 1:1 complex [LMX]. However, even with a 1:1 mole ratio of ligand to MX, the different relative solubilities of the various species in solution may result in the deposition of ionic complexes containing $[L_2M]^+$. We therefore examined the possibility that solutions containing a mole ratio of ligand to MX less than 1:1 (i.e. containing excess MX) might suppress the formation of the ionic species $[L_2M]^+$. This was found to be the case for the reaction involving CuI, where it was found to be possible to prepare a solution of CuI and TMPP in warm acetonitrile with a 2:1 CuI to TMPP mole ratio. The first product to crystallize upon cooling the reaction mixture was the desired 1:1 adduct [(TMPP)CuI], which was characterized by an X-ray structure determination and by IR and solid state ^{31}P CP MAS NMR spectroscopy, whereas solutions of 1:1 stoichiometry deposited a complex which apparently contains the $[(TMPP)_2Cu]^+$ cation (see below).

Table 3. Core Geometries for [(TMPP)CuX]

parameter	X = Cl[a]	X = Br[a]	X = I[b]
	Distances/Å		
Cu–X	2.118(2)	2.259(2)	2.417(2)
Cu–P	2.177(1)	2.197(3)	2.188(4)
P–C(11)	1.822(4)	1.815(9)	1.84(1)
P–C(21)	1.815(5)	1.828(10)	1.83(1)
P–C(31)	1.798(5)	1.796(9)	1.78(1)
Cu---O(12)	3.107(4)	3.116(8)	3.07(1)
Cu---O(22)	2.882(3)	2.887(6)	2.858(7)
Cu---O(32)	2.629(4)	2.628(7)	2.674(9)
	Angles/deg		
P–Cu–X	172.97(6)	172.00(9)	171.0(1)
Cu–P–C(11)	113.4(1)	113.9(3)	113.2(3)
Cu–P–C(21)	105.8(1)	106.5(3)	105.5(4)
Cu–P–C(31)	111.9(2)	111.2(3)	112.4(4)
C(11)–P–C(21)	111.6(2)	111.2(4)	111.5(5)
C(11)–P–C(31)	109.8(2)	109.6(4)	110.0(5)
C(21)–P–C(31)	104.1(2)	104.0(4)	103.8(5)

[a] Reference 23. [b] This work.

To date, we have been unable to prepare a solid complex between TMPP and AgI which contains the neutral 1:1 adduct [(TMPP)-AgI]. As in the case of the CuI compound described here, reaction of TMPP with AgI in acetonitrile in a 1:1 mole ratio results in the separation of an ionic complex containing the $[(TMPP)_2Ag]^+$ cation.[24,28] Similar types of product were obtained from reactions in which a 2:1 AgI to TMPP mole ratio was used.

X-ray Structure Determination. The [(TMPP)CuI] complex is isomorphous with [(TMPP)MX] (M = Cu, Ag; X = Cl, Br).[23,24] It is monomeric, with the metal atom in a nearly linear two-coordinate environment. The core geometry parameters are compared with those of the corresponding CuCl and CuBr complexes in Table 3.

[(TMPP)CuI] is the first example of a two-coordinate copper(I) iodide complex with a neutral ligand. Previously, the 1:1 complexes of tertiary phosphines with copper(I) iodide have been obtained only as tetrameric aggregates $[(PR_3)CuI]_4$ with a "cubane" (R = Et, Ph; X = Cl, Br, I)[17,31,32] or a "step" (R = Ph)[33] structure or with bulkier ligands such as tricyclohexylphosphine or tri-*o*-tolylphosphine as dimeric molecules.[34,35] The Cu–P bond length in the present compound is about 3% shorter than those in the corresponding cubane tetramers for which average values are 2.25, 2.26 Å (R = Et, Ph)[17,32] and 2% shorter than the dimeric compounds for which average values are 2.22 Å (R = cyclohexyl)[34] and 2.24 Å (R = *o*-tolyl).[35] The Cu–I bond length is 6% shorter than in the dimer molecules (average values 2.58, 2.57 Å (R = *o*-tol, cyclohexyl)) and 10% less than in the tetramer molecules (average values 2.69, 2.65 Å (R = Et, Ph)). The greater change in the case of the Cu–I bond is due to the change in bonding mode of the iodide ligand from triply bridging in the tetramers to doubly bridging in the dimers to terminal in the monomer.

While the phosphorus and halogen atoms play a dominant role in the coordination environment of the [(TMPP)MX] complexes, the methoxy oxygen atoms on the ligand could also be involved to a significant extent as well. In all cases, the conformations of

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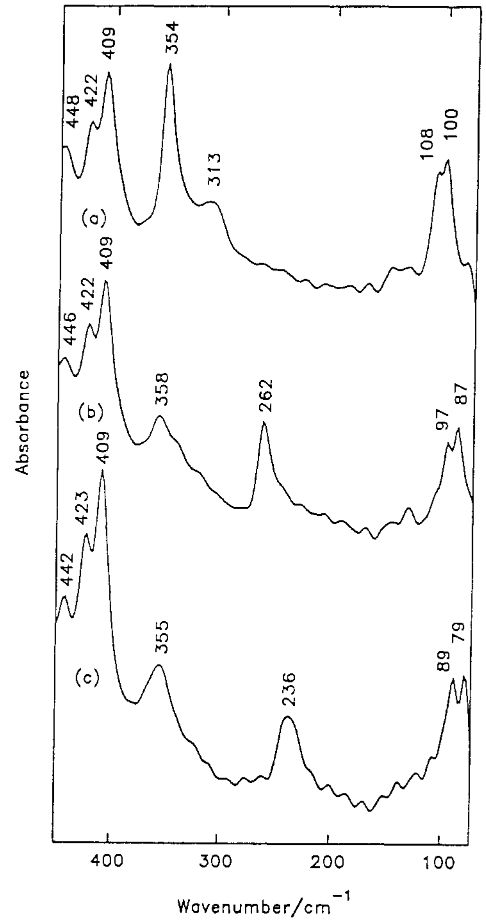

Figure 2. Far-IR spectra of [(TMPP)CuX] for (a) X = Cl, (b) X = Br, and (c) X = I.

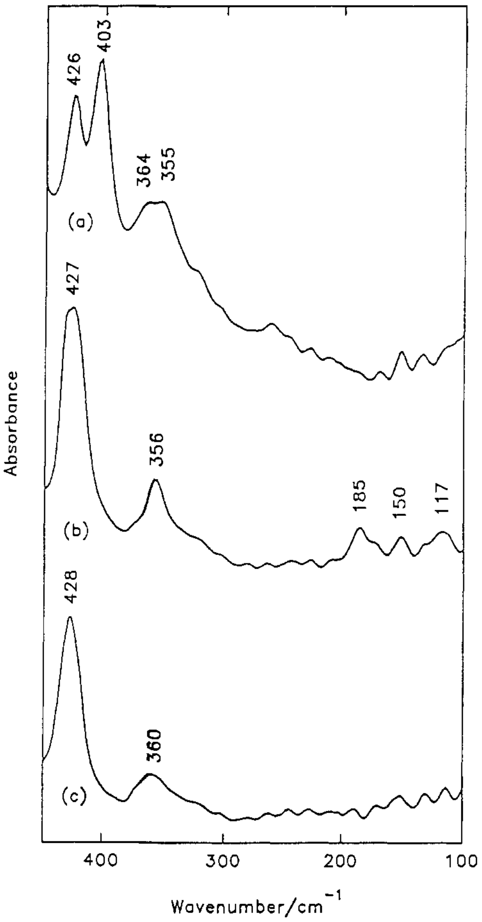

Figure 3. Far-IR spectra of (a) TMPP, (b) $[(TMPP)_2Cu]_n[Cu_nI_{2n}]$ (the product of the 1:1 TMPP/CuI reaction), and (c) $[(TMPP)_2Cu][ClO_4]$.

the phenyl rings are such that one of the *ortho*-methoxy oxygen atoms O(*n*2) is closer to the metal atom than the other two oxygens on the same ring. The resulting Cu---O(*n*2) distances are given in Table 3. The shortest of these distances is Cu---O(32), some 0.4–0.5 Å shorter than Cu---O(12). These distances are relatively long, however, supporting the view that the CuX complexes essentially involve linear P–Cu–X coordination, with only a slight perturbation by the other atoms in the ligand. The departure from linearity in the copper complexes is greater than that in [(TMPP)AgX]; P–Ag–X are 175.0(1), 174.40(6)° for X = Cl, Br, respectively,[24] only slightly more than that in $[(PMes_3)CuBr]$ (P–Cu–Br = 173.7(1)°), where the distortion is attributed to intramolecular packing effects.[22]

It is generally more difficult to achieve two-coordination at copper(I) in the presence of an iodide ligand than in the presence of chloride or bromide ligands. Thus the dihalogenocuprates(I), $[CuX_2]^-$, can be isolated as solid salts with simple tetraalkylammonium cations of moderate size for X = Cl or Br,[7] but the $[CuI_2]^-$ ion has been observed only in one compound by the use of a potassium crown ether complex as a bulky cation.[36] The majority of iodocuprate anions are isolated as oligomeric or polymeric species such as $[Cu_2I_4]^{2-}$, $[Cu_4I_6]^{2-}$, $[CuI_2]_n^{n-}$, and $[Cu_2I_3]_n^{n-}$ ($n = \infty$) with three- and four-coordinate copper.[37] The relative reluctance of CuI to form two-coordinate complexes is further illustrated by the structures of the 1:1 adducts of the sterically hindered amine ligand 2,2′,6,6′-tetramethylpiperidine with copper(I) halides. With this ligand the chloro and bromo complexes have monomeric structures with two-coordinate Cu, while the iodo complex has a dimeric halogen-bridged structure with three-coordinate Cu.[38] The fact that [(TMPP)CuI] has the same two-coordinate structure as the corresponding CuCl and CuBr compounds is thus an indication of the unusually high basicity of the ligand, which favors low coordination geometries coupled with the high degree of steric control that this ligand can exert over the coordination environment of the metal to which it is bound.

Far-IR Spectra. The far-IR spectrum of [(TMPP)CuI] is compared with those of the Cl and Br analogues in Figure 2. The weak band at 236 cm^{-1} in the spectrum of [(TMPP)CuI] is assigned as ν(CuI) by analogy to the previous assignments ν(CuX) = 354, 262 cm^{-1} for X = Cl, Br, respectively.[23] The spectrum also shows a partially resolved doublet at 79, 89 cm^{-1} which corresponds to bands at 100, 108 and 87, 97 cm^{-1} in the Cl, Br complexes, respectively. These are assigned to the bending mode δ(PCuX), and the wavenumbers may be compared with the values 109, 81, 65 cm^{-1} for the δ(XCuX) mode in $[CuX]_2^-$ for X = Cl, Br, I, respectively.[4] The δ(PCuX) mode would be doubly degenerate in the presence of 3-fold symmetry about the P–Cu–X axis; the observed splitting of this band into a doublet is attributed to the departure from 3-fold symmetry, which is caused by the slight nonlinearity of the PCuX unit in these complexes. The far-IR spectra of TMPP, the product of the 1:1 TMPP/CuI reaction (see Experimental Section), and $[(TMPP)_2Cu][ClO_4]$ are shown in Figure 3. Comparison with the results in Figure 2 shows that the ligand bands in the 400–430-cm^{-1} region show a dependence on the type of complex in which the ligand occurs. The position of the lowest wavenumber member of this set of bands increases from 403 cm^{-1} for TMPP to 409 cm^{-1} for [(TMPP)CuX] and increases still further to 427 cm^{-1} for

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Table 4. Metal–Halogen Vibrational Wavenumbers and Force Constants

	ν(CuX)/cm^{-1}			k/N m^{-1}			
	Cl	Br	I	Cl	Br	I	ref
CuX	413	313	263	228	204	173	4
$[CuX_2]^-$ [a]	405	322	279	175	157	140	4
[(TMPP)CuX]	355	262	236	169	143	139	23, *b*
$[(PPh_3)_2CuX]$	298	218	184	119	101	84	40
$[(PPh_3)_3CuX]$	214	164	138	61	56	48	40

[a] Wavenumbers for the ν_3 mode are given. [b] This work.

$[(TMPP)_2Cu][ClO_4]$. Also, while there are several bands in this region for TMPP and [(TMPP)CuX], only a single band occurs for $[(TMPP)_2Cu][ClO_4]$. The spectrum of the product of the 1:1 TMPP/CuI reaction above 300 cm^{-1} is almost identical to that of $[(TMPP)_2Cu][ClO_4]$, suggesting that the former contains the $[(TMPP)_2Cu]^+$ ion. Further support for this hypothesis comes from the ^{31}P CP MAS NMR results (see below). From this result and the overall 1:1 TMPP:CuI stoichiometry found for this complex (see Experimental Section) we formulate this complex as $[(TMPP)_2Cu]_n[Cu_nI_{2n}]$, containing a complex iodocuprate anion. The simplest structure for the anion would be linear monomeric $[CuI_2]^-$ ($n = 1$). If this anion were present, it would give rise to a band in the far-IR spectrum due to the antisymmetric ν(CuI) mode at about 280 cm^{-1}.[4] The absence of such a band (Figure 3) suggests that the structure of the anion is more complex than this, e.g. an oligomeric structure or an infinite polymeric chain structure. The spectrum of the complex also contains a number of weak bands in the 100–200-cm^{-1} region which are absent in the $[(TMPP)_2Cu][ClO_4]$ spectrum and which can therefore be assigned to the ν(CuI) modes of the complex iodocuprate anion. For such anions, the positions of the bands vary somewhat with the nature of the cation. However, for the compound $[PPh_4]_2[Cu_2I_4]$, which contains discrete $[Cu_2I_4]^{2-}$ species,[39] ν(CuI) bands occur in the far-IR at 180 and 150 cm^{-1}, and these agree well with those found for the present complex. Thus, at this stage, the most likely structural formula for the complex is $[(TMPP)_2Cu]_2[Cu_2I_4]$.

The ν(CuX) wavenumbers for the [(TMPP)CuX] complexes are compared with those of a number of related complexes in Table 4. Also given in this table are the Cu–X bond force constants, calculated in the case of the $[L_nCuX]$ species by considering the diatomic CuX unit only.[40] From these results it appears that ν(CuI) for [(TMPP)CuI] is unexpectedly high. The M–X force constants usually show a progressive decrease along the series X = Cl, Br, I, but in this case the values for X = Br, I are almost the same.

A plot of ν(CuI) vs the bond length d(CuI) for the series of $[L_nCuI]$ (n = 0–3) complexes in Table 4 is shown in Figure 4, and this shows a monotonic decrease in ν(CuI) with increasing d(CuI) which is similar in appearance to those for the corresponding Cl and Br complexes but which also indicates the unusually high value of ν(CuI) for [(TMPP)CuI].

Solid State ^{31}P CP MAS NMR Studies. The solid state NMR spectra, recorded at a field strength of 9.40 T, are shown in Figure 5, and the NMR parameters are given in Table 5. The spectra of [(TMPP)CuI] and $[(TMPP)_2Cu][ClO_4]$ each exhibit an asymmetric quartet splitting pattern of the type which has been reported previously for a range of copper(I) complexes with phosphine ligands.[17,23,29,41–43] This asymmetric splitting is due to the combined effects of scalar and dipolar spin–spin coupling between the phosphorus nucleus and the copper nucleus (^{63}Cu, ^{65}Cu; nuclear spin $I = {}^3/_2$) and the copper nuclear quadrupole coupling. The primary data reported in Table 5 are the ^{31}P chemical shifts δ and the spacings $\Delta\nu_1$, $\Delta\nu_2$, and $\Delta\nu_3$ between adjacent lines in the quartet. The parameters for [(TMPP)CuI] are very similar to those observed for the corresponding CuCl and CuBr complexes, the main difference being the slightly smaller $\Delta\nu_3/\Delta\nu_1$ value. We previously showed that this ratio is a function of the copper nuclear quadrupole coupling constant e^2qQ and is approximately proportional to the value of this coupling constant.[23] We note that $\Delta\nu_3/\Delta\nu_1$ values (and therefore the associated copper nuclear quadrupole coupling constants) for [(TMPP)CuX] show a decrease from X = Cl to X = I. The theoretical basis for this trend has been discussed,[23,44,45] and it can be noted that the same trend has been observed experimentally in the Mössbauer quadrupole splittings for the isostructural series of linear two-coordinate complexes $[(PPh_3)AuX])$.[46] ^1J(CuP) ($\Delta\nu_2$) for the $[(TMPP)_2Cu]^+$ cation is approximately 5% less than that for the [(TMPP)CuX] complexes, and this is most likely a reflection of the increase in the Cu–P distance expected in passing from the [(TMPP)CuX] complex to the sterically more crowded $[(TMPP)_2Cu]^+$ complex.

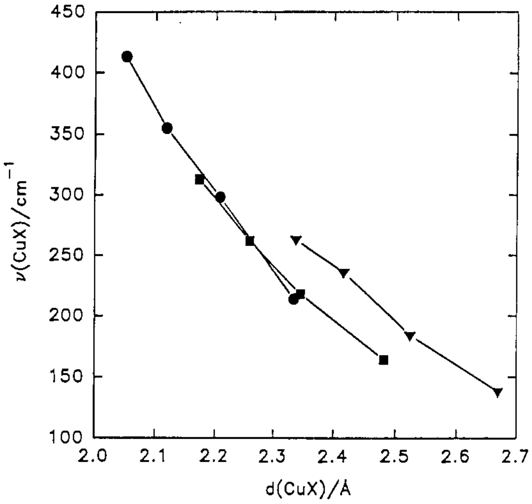

Figure 4. Plots of the ν(CuX) wavenumber *vs* the Cu–X bond length d(CuX) for (in ascending order of d(CuX)) CuX(vapor), [(TMPP)-CuX], $[(PPh_3)_2CuX]$, and $[(PPh_3)_3CuX]$. X = Cl (●), Br (■), I (▼).

Table 5. Solid State CP MAS ^{31}P NMR Chemical Shifts δ (ppm with Reference to 85% H_3PO_4) and Line Spacings $\Delta\nu_i$ (kHz) at B = 9.40 T

complex	δ	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\Delta\nu_3/\Delta\nu_1$
$[(TMPP)_2Cu]_n[Cu_nI_{2n}]$ [a]	−80	1.34	1.98	2.20	1.64
$[(TMPP)_2Cu][ClO_4]$	−80	1.35	2.02	2.19	1.62
[(TMPP)CuCl]	−63	1.60	2.15	2.40	1.50
[(TMPP)CuBr]	−63	1.64	2.16	2.36	1.44
[(TMPP)CuI]	−63	1.62	2.10	2.30	1.42

[a] Average parameters for two almost coincident quartets.

The spectrum of the compound formulated as $[(TMPP)_2Cu]_n[Cu_nI_{2n}]$ consists of a superposition of two almost coincident quartet patterns. The chemical shift and the quartet line spacings are very similar to those observed for $[(TMPP)_2Cu][ClO_4]$, and this provides strong support for the proposed presence of the $[(TMPP)_2Cu]^+$ cation in this complex.

Comparison of the results obtained in the present study with those obtained for related complexes demonstrates the strong dependence of the splitting ratio $\Delta\nu_3/\Delta\nu_1$ on the copper coordina-

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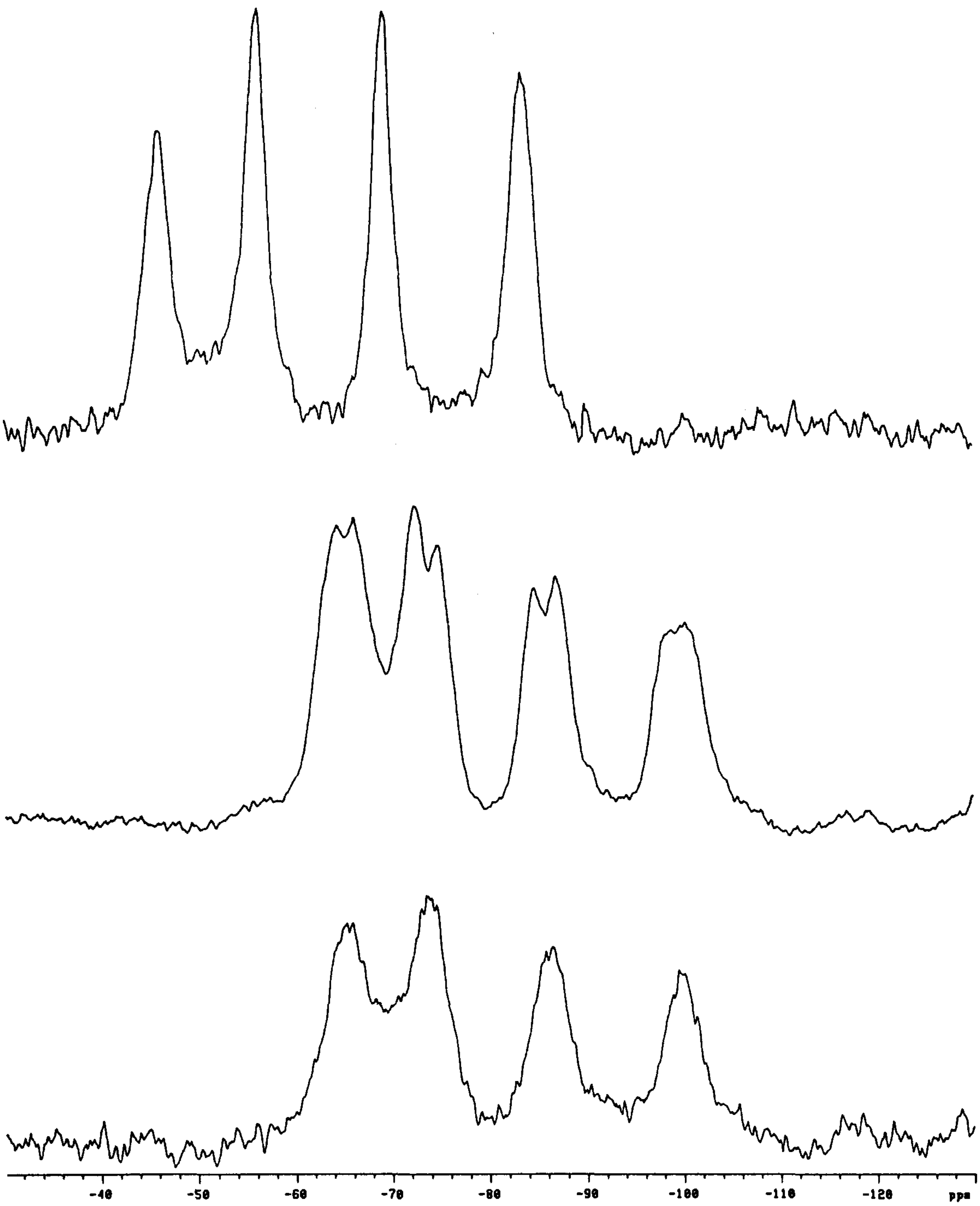

Figure 5. ^{31}P CP MAS NMR spectra of [(TMPP)CuI] (top), $[(TMPP)_2Cu]_n[Cu_nI_{2n}]$ (middle), and $[(TMPP)_2Cu][ClO_4]$ (bottom).

tion environment. 1:1 complexes of tertiary phosphines with copper(I) halides form monomeric or oligomeric structures $[LCuX]_n$ in which the copper coordination number (CN) decreases with decreasing *n*. For the monomers [(TMPP)CuX] (CN = 2) the $\Delta\nu_3/\Delta\nu_1$ ratio lies in the range 1.4–1.5 for field strength $B = 9.4$ T (Table 5). For the dimers $[P(o\text{-tol})_3CuX]_2$ (CN = 3) the ratio at this field strength is about 1.3, while for the cubane tetramers $[(PPh_3)CuX]_4$ (CN = 4) it is less than 1.2.[35] This corresponds to an increase in the copper nuclear quadrupole coupling constant with decreasing coordination number. It has previously been shown that the electric field gradient, which is responsible for the nuclear quadrupole coupling in copper(I) complexes, is determined primarily by contributions from electron density in the copper 4p orbitals.[45] The 4p electron imbalance increases as the copper coordination number decreases, becoming a maximum at coordination number 2. This results in an increase in the coupling constant with decreasing coordination number. There is a further increase in the $\Delta\nu_3/\Delta\nu_1$ ratio in going from the neutral [(TMPP)CuX] to the ionic $[(TMPP)_2Cu]^+$ complexes. This can readily be accounted for in terms of the electronic structures of the species concerned. The replacement of the halide ligand (a weak σ-donor) in [(TMPP)CuX] by the phosphine ligand (a stronger σ-donor) to produce $[(TMPP)_2Cu]^+$ results in an increase in the population of the Cu $4p_z$ orbital and thus to an increase in the copper nuclear quadrupole coupling constant. A similar situation has previously been found in the case of linear gold(I) complexes where, for example, the Mössbauer quadrupole splitting for $[(PPh_3)_2Au]^+$ (9.43 mm s^{-1})[47]

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is larger than that for [$(PPh_3)AuCl$] (7.53 mm s^{-1})[48] or for [$(PPh_3)AuI$] (7.36 mm s^{-1}).[46]

The ^{63}Cu nuclear quadrupole coupling constant e^2qQ/h for the two ionic complexes, estimated from the asymmetry of the quartet splitting patterns,[23,43] is greater than 70 MHz. This is higher than any value reported to date for a copper(I) complex.[4,43]

The observation of two quartet patterns in the spectrum of [$(TMPP)_2Cu]_n[Cu_nI_{2n}$] is indicative either of the presence of inequivalent P atoms within the [$(TMPP)_2Cu]^+$ ion or of the presence of inequivalent [$(TMPP)_2Cu]^+$ ions in the solid. The absence of splitting observed in the, albeit broad, spectrum of the [$(TMPP)_2Cu][ClO_4$] complex suggests a similar situation is possible for the present copper sample, and this is consistent with the assignment of the complex as [$(TMPP)_2Cu]_2[Cu_2I_4$], suggested by the far-IR results. However, it should be noted that while a similar splitting was observed in the spectrum of the corresponding AgI system, a single-crystal structure determined for one crystal obtained from this material was characterized as [$(TMPP)_2Ag]_2[Ag_5I_7$].

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Supplementary Material Available: For the crystal structure study, listings of crystal and refinement data, H atom coordinates, thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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