

vations made in this study are in poor agreement with previous reports for other oxonium salts and cast some doubt on the general validity of some of the previous conclusions. Due to their good thermal stability, oxonium salts of complex fluoro cations are well suited for further experimental studies.

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**Registry No.**  $\text{OH}_3^+\text{AsF}_6^-$ , 21501-81-5;  $\text{OD}_3^+\text{AsF}_6^-$ , 92186-28-2;  $\text{O}_2^+\text{AsF}_6^-$ , 12370-43-3;  $\text{OD}_3^+\text{SbF}_6^-$ , 92186-29-3;  $\text{OH}_3^+\text{SbF}_6^-$ , 55649-03-1;  $\text{D}_2\text{O}$ , 7789-20-0;  $\text{DF}$ , 14333-26-7;  $\text{AsF}_5$ , 7784-36-3;  $\text{SbF}_5$ , 7783-70-2;  $\text{OD}_2\text{H}^+\text{SbF}_6^-$ , 92186-30-6;  $\text{ODH}_2^+\text{SbF}_6^-$ , 92186-31-7;  $\text{OD}_3^+$ , 24847-51-6;  $\text{MoF}_4\text{O}$ , 14459-59-7;  $\text{D}_2$ , 7782-39-0.

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## Lewis Base Adducts of Group 1B Metal(I) Compounds. 8. High-Resolution Solid-State $^{31}\text{P}$ Nuclear Magnetic Resonance Spectra of Tetrameric (Triphenylphosphine)copper(I) Halide Complexes and Crystal Structure Determination of Cubane $[\text{PPh}_3\text{CuBr}]_4$

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Crystal structure analysis of the tetrameric 1:1 adduct of  $\text{PPh}_3$  with  $\text{CuBr}$ ,  $[\text{CuBrPPh}_3]_4$ , recrystallized from refluxing toluene, shows that it has crystallized in a "cubane" rather than the previously recorded "step" form. A residual of 0.044 was obtained for 3708 independent observed diffractometer reflections recorded at 295 K after full-matrix least-squares refinement; crystals are isomorphous with the chloride, with an orthorhombic  $Pbcn$  cell,  $a = 17.662$  (5) Å,  $b = 20.748$  (7) Å,  $c = 18.351$  (6) Å, and  $Z(\text{tetramer}) = 4$ . The existence of the cubane form of the bromide was discovered during high-resolution solid-state  $^{31}\text{P}$  NMR spectral studies on a series of cuprous halide-triphenylphosphine complexes.

### Introduction

Modern structural studies of the tetrameric 1:1 adducts of copper(I) and silver(I) halides with triphenylphosphine have shown that while the copper(I) chloride adduct crystallizes in a "cubane" form,<sup>2</sup> the bromide and iodide adducts both crystallize as "step" structures.<sup>3,4</sup> The analogous silver(I) adducts all crystallize as cubane structures;<sup>5-7</sup> the iodide, however, can also be induced to crystallize in the step form.<sup>7</sup> The step structure is less sterically constrained than the cubane structure and is postulated to be the preferred structural form for combinations with large halide and ligand molecules.<sup>7</sup> However, the reported cubane structure for the adduct of copper(I) iodide with sterically demanding ligands,<sup>8,9</sup> the existence of step and cubane structures for the silver complexes mentioned above, and evidence that  $[\text{AsPh}_3\text{CuI}]_4$  exists in both forms<sup>10</sup> suggest that both types of structures can accommodate wide variations in electronic and steric properties of the constituent molecules and that it may be possible to crystallize both forms for some adducts with only small changes in experimental conditions.

As part of a program investigating the high-resolution solid-state NMR spectra of complexes of univalent group 1B metals, we recorded the  $^{31}\text{P}$  spectra of  $[\text{PPh}_3\text{CuCl}]_4$ ,  $[\text{PPh}_3\text{CuBr}]_4$ , and  $[\text{PPh}_3\text{CuI}]_4$ , prepared according to literature methods.<sup>11</sup> Similarities between the spectra of the chloride

and bromide complexes suggested that they could be isostructural, giving rise to the possibility that one of them could be induced to crystallize in both cubane and step forms. Subsequent structural determination of the bromide complex showed that it, in fact, had crystallized in the cubane form. In this report we describe the  $^{31}\text{P}$  solid-state NMR results for these compounds and the determination of the crystal and molecular structure of cubane  $[\text{PPh}_3\text{CuBr}]_4$ .

### Experimental Section

$^{31}\text{P}$  NMR spectra were obtained on a Bruker CXP-300 spectrometer at 121.47 MHz using  $^1\text{H}$ - $^{31}\text{P}$  cross polarization with rf fields of 8 and 20 G for  $^1\text{H}$  and  $^{31}\text{P}$ , respectively. Single contacts of 1 ms were used with spin temperature alternation and recycle times of between 10 and 50 s, depending on the  $^1\text{H}$  spin lattice relaxation times. Samples were packed in Delrin rotors and spun at speeds of between 3.0 and 4.0 kHz at the magic angle. A sweep width of 20 kHz with a total acquisition time of 12.8 ms was used. Between 20 and 200 FID's were collected, zero filled to 8 K, and transformed with an experimental line broadening of 10-50 Hz. Chemical shift data are referenced to 85% phosphoric acid.

**Crystal Data:**  $\text{C}_{72}\text{H}_{60}\text{Br}_4\text{Cu}_4\text{P}_4$ ,  $M_r = 1623$ , orthorhombic, space group  $Pbcn$  ( $D_{2h}^{14}$ , No. 60),  $a = 17.662$  (5) Å,  $b = 20.748$  (7) Å,  $c = 18.351$  (6) Å,  $V = 6724$  (4) Å<sup>3</sup>,  $D_{\text{measd}} = 1.61$  (1),  $D_{\text{calcd}} (Z = 4) = 1.60$  g cm<sup>-3</sup>,  $F(000) = 3232$ ; monochromatic  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu_{\text{Mo}} = 39.5$  cm<sup>-1</sup>; prism,  $0.10 \times 0.10 \times 0.42$  mm (capillary),  $T = 295$  K.  $A^*_{\text{min}} = 1.31$ ,  $A^*_{\text{max}} = 1.40$ .

**Structure Determination.** A unique data set was measured to  $2\theta_{\text{max}} = 50^\circ$  on a Syntex P2<sub>1</sub> four-circle diffractometer in conventional  $2\theta/\theta$  scan mode. A total of 5966 independent reflections were obtained, 3708 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; ( $x, y, z, U_{\text{iso}}\text{H}$ ) were included constrained at idealized values. Residuals ( $R, R'$ ) at convergence (on  $|F|$ ) were 0.044 and 0.047, reflection weights being  $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$ . Neutral

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Table I. Non-Hydrogen Atom Coordinates

atom	x	y	z
Cu(1)	0.09607 (7)	0.43293 (6)	0.22246 (7)
Cu(2)	0.04640 (8)	0.32764 (6)	0.33128 (7)
Br(1)	0.09514 (6)	0.30942 (5)	0.20561 (6)
Br(2)	0.03189 (6)	0.44884 (4)	0.34364 (5)
P(1)	0.2066 (1)	0.4752 (1)	0.1927 (1)
P(2)	0.0801 (2)	0.2740 (1)	0.4299 (1)
C(1)	0.2894 (6)	0.4329 (5)	0.2304 (6)
C(2)	0.3463 (7)	0.4642 (6)	0.2663 (6)
C(3)	0.4069 (8)	0.4301 (8)	0.2955 (8)
C(4)	0.4092 (8)	0.3653 (9)	0.2876 (9)
C(5)	0.3535 (8)	0.3318 (6)	0.2526 (10)
C(6)	0.2929 (6)	0.3671 (6)	0.2245 (8)
C(7)	0.2237 (5)	0.5591 (4)	0.2185 (5)
C(8)	0.1938 (5)	0.5814 (5)	0.2826 (6)
C(9)	0.2111 (7)	0.6436 (6)	0.3079 (6)
C(10)	0.2575 (8)	0.6818 (5)	0.2670 (7)
C(11)	0.2871 (8)	0.6604 (6)	0.2012 (8)
C(12)	0.2693 (7)	0.5991 (5)	0.1784 (7)
C(13)	0.2259 (6)	0.4777 (4)	0.0949 (5)
C(14)	0.1695 (6)	0.5032 (6)	0.0517 (6)
C(15)	0.1849 (8)	0.5127 (7)	-0.0211 (8)
C(16)	0.2541 (10)	0.4974 (8)	-0.0505 (7)
C(17)	0.3082 (8)	0.4693 (6)	-0.0093 (7)
C(18)	0.2949 (6)	0.4602 (5)	0.0648 (6)
C(19)	0.1805 (5)	0.2625 (5)	0.4492 (5)
C(20)	0.2273 (7)	0.3134 (6)	0.4350 (7)
C(21)	0.3011 (8)	0.3125 (6)	0.4590 (9)
C(22)	0.3292 (7)	0.2599 (7)	0.4930 (9)
C(23)	0.2847 (7)	0.2062 (6)	0.5049 (7)
C(24)	0.2102 (6)	0.2084 (5)	0.4834 (6)
C(25)	0.0406 (5)	0.1929 (4)	0.4314 (6)
C(26)	0.0340 (7)	0.1608 (6)	0.3659 (7)
C(27)	0.0019 (11)	0.1005 (7)	0.3620 (9)
C(28)	-0.0214 (8)	0.0701 (6)	0.4226 (11)
C(29)	-0.0185 (8)	0.1009 (6)	0.4890 (9)
C(30)	0.0143 (7)	0.1626 (5)	0.4937 (7)
C(31)	0.0491 (6)	0.3104 (5)	0.5150 (6)
C(32)	0.0828 (7)	0.3029 (6)	0.5817 (6)
C(33)	0.0587 (8)	0.3332 (7)	0.6434 (7)
C(34)	-0.0020 (8)	0.3738 (6)	0.6393 (6)
C(35)	-0.0386 (7)	0.3827 (5)	0.5749 (7)
C(36)	-0.0126 (6)	0.3517 (5)	0.5116 (6)

complex scattering factors were used;<sup>12</sup> computation used the X-RAY 76 program system<sup>13</sup> implemented by S. R. Hall on a Perkin-Elmer 3240 computer. Refinement was initiated by using the coordinate setting and atom numbering used elsewhere for the chloride analogue.<sup>2</sup>

### Discussion

The structure determination is consistent with the proposed 1:1 CuBr:PPh<sub>3</sub> stoichiometry; the isomorphism with the structure of the previously studied chloride analogue,<sup>2</sup> with the subsequent geometrical detail, establishes unequivocally that the complex is of the cubane tetramer form (Figure 1). From (i) the observation of this complex and its iodide analogue to exhibit the step structure in their previously studied crystalline forms, together with (ii) the observation of cubane structures with the less sterically demanding triethylarsine and -phosphine ligands and (iii) the observation of a cubane structure across the whole spectrum of 1:1 adducts of triphenylphosphine with silver chloride, bromide, and iodide, albeit distorted, and in the case of the iodide capable of independent existence in the step form as well, it has been suggested that the nature of the isomer obtained is determined by the strength of intramolecular van der Waals interactions, increased repulsion favoring the less crowded step structure.<sup>7</sup> While the result of the present study simply develops the gray area at the boundary where both isomers may be found, it also

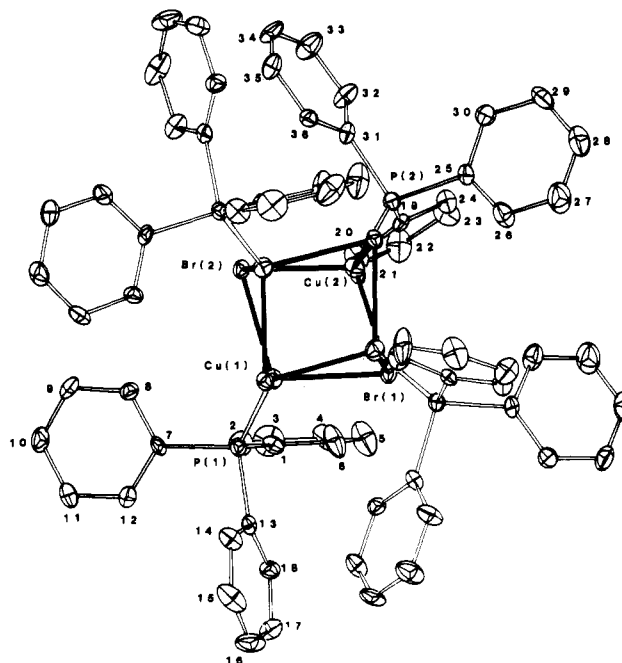


Figure 1. Projection of the cubane tetramer of [CuBrPPh<sub>3</sub>]<sub>4</sub> showing the non-hydrogen atom labeling and 20% thermal ellipsoids.

suggests that, in these areas, additional factors such as the nature of the crystallization solvent (chloroform/ether for cubane [Ag<sub>4</sub>I<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>], methylene chloride/ether for step [Ag<sub>4</sub>I<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>],<sup>7</sup> chloroform for step [Cu<sub>4</sub>Br<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>],<sup>2</sup> toluene for cubane [Cu<sub>4</sub>Br<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>], may be an ultimate marginal determinant, perhaps with the more polar solvents favoring the more accessibly solvatable step structure. A similarly sensitive isomerism has been observed with the 1:1 copper(I) iodide:pyridine complex, which exists in both cubane tetramer<sup>14</sup> and "stair polymer" forms,<sup>15</sup> the latter seemingly being the pyridine base equivalent of the step structure, which is only recorded so far for phosphine and arsine base 1:1 complexes with copper and silver halides. [The step structure is known for pyridine base adducts of stoichiometry other than 1:1, however.<sup>9</sup>]

Given the borderline nature of the present complex in respect to the cubane/step isomerism, it might be expected that, in consequence of postulated increases in steric strain, strain within the cube might be unusually large and be manifested in unusually large distortions and/or abnormally long copper-copper distances. Certainly in respect of these, the variations in copper-copper distance on passing from the chloride to the bromide are not monotonic (Table II), the shortest distance in the former (3.112 (1) Å) diminishing to 3.087 (2) Å on passing to the bromide, while the three long distances all increase substantially. The latter (3.404 (2)–3.541 (2) Å) are all very much longer than the value of 3.184 (2) Å found in the highly symmetrical [Cu<sub>4</sub>Br<sub>4</sub>(PEt<sub>3</sub>)<sub>4</sub>] cubane structure,<sup>16</sup> as is the mean of all distances (3.34<sub>5</sub> Å; cf. the chloride also 3.30<sub>6</sub> Å).

The solid-state <sup>31</sup>P NMR spectra for cubane [CuClPPh<sub>3</sub>]<sub>4</sub>, cubane and step [CuBrPPh<sub>3</sub>]<sub>4</sub>, and step [CuIPPh<sub>3</sub>]<sub>4</sub> are reproduced in Figure 2. Previous solid-state studies on copper(I) triphenylphosphine complexes have postulated that coupling between the phosphorus and quadrupolar copper nuclei causes the resonance line of each crystallographically independent

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Table II. Molecular Core Geometry (Parameters for the Chloride Analogue Given in Parentheses)<sup>a</sup>

Distances (Å)		
Cu(1)··Cu(1')	3.541 (2)	(3.430 (2))
Cu(1)··Cu(2)	3.087 (2)	(3.118 (1))
Cu(1)··Cu(2')	3.475 (2)	(3.417 (1))
Cu(2)··Cu(2')	3.404 (2)	(3.337 (2))
Cu(1)-Br(1)	2.581 (2)	(2.497 (2))
Cu(1)-Br(2)	2.518 (2)	(2.409 (2))
Cu(1)-Br(2')	2.586 (2)	(2.434 (2))
Cu(2)-Br(1)	2.491 (2)	(2.363 (2))
Cu(2)-Br(1')	2.617 (2)	(2.505 (2))
Cu(2)-Br(2)	2.538 (2)	(2.457 (2))
Cu(1)-P(1)	2.209 (3)	(2.193 (2))
Cu(2)-P(2)	2.206 (3)	(2.192 (2))
P(1)-C(1)	1.841 (11)	(1.835 (7))
P(1)-C(7)	1.830 (10)	(1.825 (7))
P(1)-C(13)	1.827 (10)	(1.810 (7))
P(2)-C(19)	1.824 (10)	(1.816 (7))
P(2)-C(25)	1.821 (10)	(1.805 (7))
P(2)-C(31)	1.818 (10)	(1.834 (7))
Angles (deg)		
Br(1)-Cu(1)-Br(2)	103.49 (5)	(98.69 (6))
Br(1)-Cu(1)-Br(2')	93.73 (5)	(92.26 (6))
Br(2)-Cu(1)-Br(2')	90.24 (6)	(88.94 (6))
Br(1)-Cu(2)-Br(2)	105.55 (6)	(101.11 (7))
Br(1)-Cu(2)-Br(1')	93.94 (6)	(92.21 (6))
Br(2)-Cu(2)-Br(1')	94.00 (6)	(91.53 (6))
Cu(1)-Br(1)-Cu(2)	74.96 (5)	(79.75 (6))
Cu(1)-Br(1)-Cu(2')	83.90 (5)	(86.18 (6))
Cu(2)-Br(1)-Cu(2')	83.54 (5)	(86.49 (6))
Cu(1)-Br(2)-Cu(2)	75.26 (5)	(79.71 (6))
Cu(1)-Br(2)-Cu(1')	87.85 (5)	(90.19 (6))
Cu(2)-Br(2)-Cu(1')	85.40 (5)	(88.66 (6))
P(1)-Cu(1)-Br(1)	111.73 (8)	(112.73 (7))
P(1)-Cu(1)-Br(2)	124.36 (10)	(125.02 (8))
P(1)-Cu(1)-Br(2')	127.27 (9)	(131.06 (8))
P(2)-Cu(2)-Br(1)	126.15 (9)	(129.17 (8))
P(2)-Cu(2)-Br(2)	116.99 (9)	(118.28 (7))
P(2)-Cu(2)-Br(1')	113.37 (9)	(115.87 (7))
Cu(1)-P(1)-C(1)	114.8 (4)	(114.2 (2))
Cu(1)-P(1)-C(7)	117.4 (3)	(118.1 (2))
Cu(1)-P(1)-C(13)	114.8 (3)	(114.9 (2))
C(1)-P(1)-C(7)	103.0 (5)	(102.4 (3))
C(1)-P(1)-C(13)	103.6 (5)	(104.0 (3))
C(7)-P(1)-C(13)	101.3 (4)	(101.3 (3))
Cu(2)-P(2)-C(19)	119.1 (3)	(120.0 (2))
Cu(2)-P(2)-C(25)	112.0 (3)	(111.7 (2))
Cu(2)-P(2)-C(31)	114.4 (3)	(113.9 (2))
C(19)-P(2)-C(25)	104.4 (4)	(104.5 (3))
C(19)-P(2)-C(31)	100.4 (4)	(100.1 (3))
C(25)-P(2)-C(31)	104.8 (5)	(105.1 (3))

<sup>a</sup> Primed atoms are generated by the transformation ( $\bar{x}$ ,  $y$ ,  $1/2 - z$ ).

phosphorus atom to split into four peaks, with variation in the splitting between lines being ascribed to the failure of the magic-angle-spinning technique to average out the Cu-P dipolar and J tensor interactions. Large differences in splitting values are correlated with low local symmetry around the copper atom.<sup>17,18</sup> In accordance with this earlier work, the present eight-line spectra observed for the cubane chloride and bromide compounds can be interpreted as arising from the splitting into quartets of each of the phosphorus resonance lines of the two crystallographically independent but chemically similar phosphorus atoms found in the *Pbcn* cubane structure. The magnitude of and the differences in splittings between the lines of each set of quartets [Cl (1750, 2000, 2140 Hz; 1670, 2020, 2140 Hz); Br (1710, 1910, 2000 Hz; 1690, 1910, 2030 Hz)] are in accord with the relatively short Cu-P bond lengths (~2.2 Å) of the cubane structures and the considerable dis-

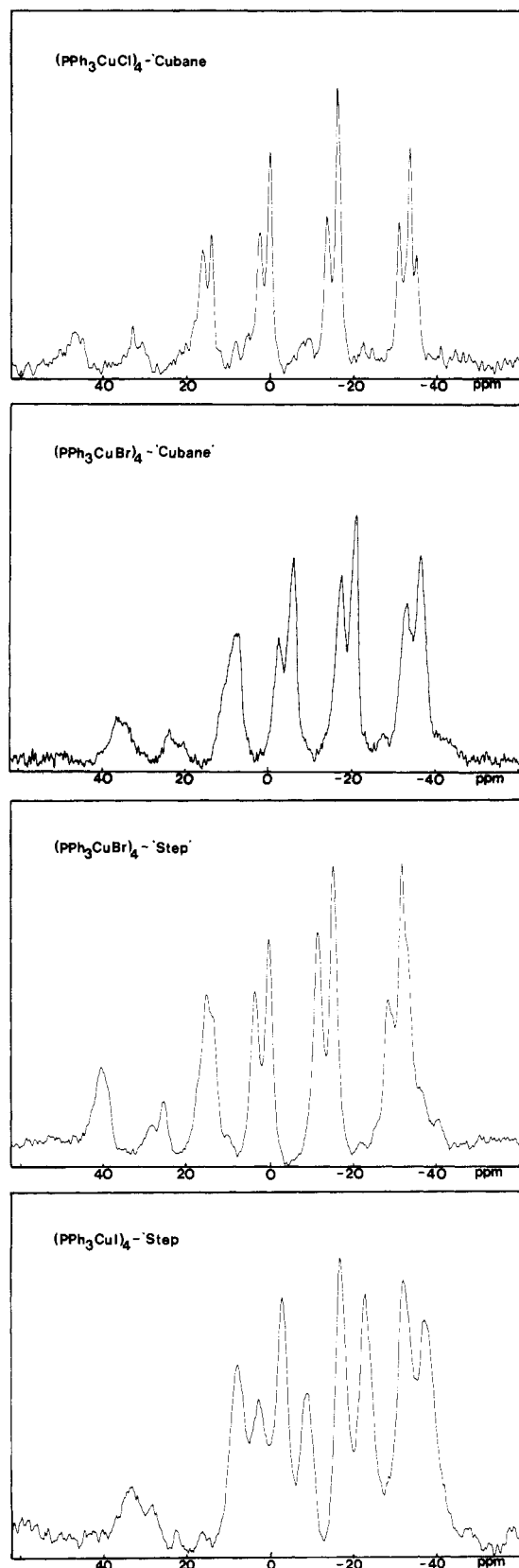


Figure 2. <sup>31</sup>P NMR spectra of cubane [CuClPPh<sub>3</sub>]<sub>4</sub> and [CuBrPPh<sub>3</sub>]<sub>4</sub> and step [CuBrPPh<sub>3</sub>]<sub>4</sub> and [CuIPPh<sub>3</sub>]<sub>4</sub>. The spinning side bands observed on either side of the main signal indicate the existence of considerable <sup>31</sup>P chemical shift anisotropy. Small satellite peaks observed on the main high-field peaks have been attributed to resolution of the <sup>65</sup>Cu isotope peaks.<sup>17,18</sup>

ortion of the first coordination sphere of the copper atom (I<sub>3</sub>CuP) from tetrahedral symmetry. [Cf. PPh<sub>3</sub>CuX (X = Cl, Br, I): Cu-P = ~2.35 Å,<sup>19</sup> symmetry of P<sub>3</sub>CuX core ~C<sub>3v</sub>.

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Splitting of principal quartets: Cl, 930, 920, 910 Hz; Br, 960, 940, 930 Hz; I, 900, 930, 920 Hz.<sup>18,20]</sup> In the step structure, the two crystallographically independent phosphorus atoms are bonded to three- and four-coordinate copper, respectively. Nevertheless, the splittings for each of the observed quartets are of the same order of magnitude and are, in fact, very similar to those observed for the cubane isomers: Br, (1650, 1930, 2000 Hz; 1440, 1820, 2080 Hz); I, (1350, 1740, 1850 Hz; 1410, 1750, 1820 Hz). These results suggest that the coordination number of the bonded copper atom is not a major factor in determining the magnitude of the quadrupolar splitting of the phosphorus resonance signal. In this context, it is of interest to note the similarity of the Cu-P bond lengths

observed for each of these four structures: Cl (cubane), 2.193 (2), 2.192 (2) Å; Br (cubane), 2.209 (3), 2.206 (3) Å; Br (step), 2.194 (4), 2.207 (3) Å; I (step), 2.228 (5), 2.242 (4) Å.

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**Registry No.** [CuClPPh<sub>3</sub>]<sub>4</sub> (cubane), 50409-58-0; [CuBrPPh<sub>3</sub>]<sub>4</sub> (cubane), 92011-27-3; [CuBrPPh<sub>3</sub>]<sub>4</sub> (step), 50576-71-1; [CuIPPh<sub>3</sub>]<sub>4</sub> (step), 53432-64-7.

**Supplementary Material Available:** Listings of anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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 (20) Barron, P. F.; Dyason, J. C.; Healy, P. C., unpublished data.

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## Lewis Base Adducts of Group 1B Metal(I) Compounds. 9. Synthesis and Crystal Structures of Adducts of Copper(I) Thiocyanate with Substituted Pyridine Bases

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The crystal structures of the title compounds, Cu(SCN)L, L = 2-methylpyridine (1), 2,6-dimethylpyridine (2), and Cu(SCN)L<sub>2</sub>, L = 2-, 3-, and 4-methylpyridine (3-5, respectively), 2,4-dimethylpyridine (6), quinoline (7), have been established by single-crystal X-ray diffraction at 295 K and refined by full-matrix least squares to residuals of 0.026, 0.039, 0.048, 0.032, 0.054, 0.058, and 0.029 for 1164, 1339, 1499, 1731, 903, 1748 and 468 independent "observed" reflections, respectively. Crystals of 1 are triclinic, *P*1̄, with *a* = 9.452 (3) Å, *b* = 8.077 (3) Å, *c* = 5.779 (1) Å,  $\alpha$  = 104.33 (2)°,  $\beta$  = 96.64 (2)°,  $\gamma$  = 100.83 (3)°, and *Z* = 2; the structure is a polymer consisting of pairs of CuL(SCN)CuL(SCN) strands linked by centrosymmetric four-membered Cu<sub>2</sub>S<sub>2</sub> and eight-membered Cu(SCN)<sub>2</sub>Cu rings. Crystals of 2 are monoclinic, *P*2<sub>1</sub>/*c*, with *a* = 7.721 (2) Å, *b* = 7.753 (2) Å, *c* = 16.113 (4) Å,  $\beta$  = 90.67 (2)°, and *Z* = 4; the structure is a single-stranded polymer—CuL(SCN)CuL(SCN). Crystals of 3 are orthorhombic, *F*dd2, with *a* = 43.68 (1) Å, *b* = 16.402 (4) Å, *c* = 8.064 (3) Å, and *Z* = 16. Crystals of 4 are monoclinic, *P*2<sub>1</sub>/*n*, with *a* = 17.68 (1) Å, *b* = 5.874 (4) Å, *c* = 14.367 (8) Å,  $\beta$  = 112.91 (4)°, and *Z* = 4. Crystals of 5 are monoclinic, *P*2<sub>1</sub>, with *a* = 14.59 (2) Å, *b* = 5.823 (6) Å, *c* = 8.953 (10) Å,  $\beta$  = 106.44 (10)°, and *Z* = 2. Crystals of 6 are monoclinic, *P*2<sub>1</sub>/*c*, with *a* = 28.93 (3) Å, *b* = 5.867 (4) Å, *c* = 20.19 (3) Å,  $\beta$  = 112.70 (8)°, and *Z* = 8. Crystals of 7 are orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with *a* = 16.219 (4) Å, *b* = 12.838 (3) Å, *c* = 8.032 (2) Å, and *Z* = 4. In spite of the diverse crystal symmetries found for 3-7, all contain single-stranded CuL<sub>2</sub>(SCN)CuL<sub>2</sub>(SCN)CuL<sub>2</sub> polymers, with different conformational types. All complexes were synthesized by reaction of copper(I) thiocyanate with the parent base, with or without the presence of acetonitrile as solvent.

### Introduction

In an earlier report,<sup>2</sup> in our series of studies on the nature of adducts formed by the crystallization of group 1B metal(I) halides/pseudohalides from, or in the presence of, nitrogen bases, we have described the isolation and structure determination of the 1:1 adducts of silver(I) thiocyanate with 2- and 3-methylpyridine and 2,6-dimethylpyridine and the 1:2 adduct with quinoline; in all cases recrystallization was carried out from the pure base. Following this study with pyridine bases variously substituted in the 2- and 6-positions, we now turn to consider a similar array of derivatives obtained by the recrystallization of copper(I) thiocyanate from such bases or in the presence of acetonitrile as solvent. With use of 2-, 3-, and 4-methylpyridine, 2,4-dimethylpyridine, and quinoline, crystalline derivatives have been obtained from solutions of copper(I) thiocyanate in the pure base at room temperature, all being found to have 1:2 stoichiometry. With 2-methyl-

pyridine in the presence of acetonitrile as solvent, a 1:1 adduct has also been obtained; a 1:1 adduct has also been obtained by the recrystallization of copper(I) thiocyanate from 2,6-dimethylpyridine. Structure determinations using single-crystal X-ray diffraction techniques have in all cases been carried out on material sealed in capillaries, since the base in complexes of this type is readily lost on exposure to the atmosphere. Abbreviations used are as follows: py, pyridine; quin, quinoline.

### Crystallography

Following an initial photographic examination to establish approximate cell dimensions, probable space group (ultimately justified by solution), and the extent of available data, unique data sets were measured within a predetermined  $2\theta_{\max}$  limit with Syntex P1 and P2<sub>1</sub> four-circle diffractometers fitted with graphite-monochromated radiation sources ( $\lambda_{Mo}$  = 0.7106, Å) in conventional  $2\theta/\theta$  scan mode at 295 K. *N* independent reflections were obtained, *N*<sub>0</sub> with  $I > 3\sigma(I)$  being considered "observed" and used in the full-matrix least-squares refinement after solution of the structure by vector methods. Unless stated otherwise, analytical absorption corrections were applied. Non-hydrogen-atom thermal parameters were refined with an an-

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 (2) Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1984, 229.