Inorg. Chem. 1991, 30, 4743-4753

Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557,
University of Auckland, Private Bag, Auckland, New Zealand, University of Warwick, Coventry CV4 7AL, England, and
Colorado State University, Fort Collins, Colorado 80523, and JEOL NMR Applications Laboratory, Peabody, Massachusetts 91960

Phosphole Complexes of Copper(I) Halides. Investigations of Structure and Bonding by X-ray Crystallography, Infrared Spectroscopy, and CP/MAS ^{31}P NMR Spectroscopy

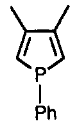
Saeed Attar,[1a] Graham A. Bowmaker,[1b] Nathaniel W. Alcock,[1c] James S. Frye,[1d] William H. Bearden,[1e]
and John H. Nelson*,[1a]

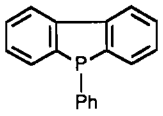
Received July 3, 1991

A series of complexes of 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP), of the type $[L_nCuX]_m$ ($n = 1$, $m = 4$, L = DMPP, DBP; $n = 2$, $m = 2$, L = DMPP; $n = 3$, $m = 1$, L = DMPP, DBP; X = Cl, Br, I) have been prepared and characterized. The structure of $[(DMPP)CuI]_4$ has been determined by X-ray crystallography. It crystallizes in the space group $C2/c$ with $a = 21.058$ (4) Å, $b = 12.059$ (2) Å, $c = 23.425$ (7) Å, $\beta = 111.50$ (2)°, and $Z = 4$. The structure was refined by least-squares methods with $R(F) = 0.037$ for 2845 unique reflections with $I/\sigma(I) \geq 3.0$. The complex crystallizes as a tetramer $[(DMPP)CuI]_4$ with the cubane structure which has previously been observed for 1:1 complexes of PPh_3 and other phosphine and amine ligands with copper(I) halides. In this structure each of the four copper atoms is tetracoordinated through bonds to the P atom of the phosphole ligand and the three bridging iodine atoms, which are in turn tricoordinated. The complex lies on a crystallographic C_2 axis. The average bond lengths in the $P_4Cu_4I_4$ core are Cu–P = 2.253, Cu–I = 2.684, and Cu- - -Cu = 2.933 Å, and the average bond angles are Cu–I–Cu = 65.92, I–Cu–I = 109.35, and P–Cu–I = 109.55°. The structures of the other members of the series were deduced from their far-IR and cross-polarization magic-angle-spinning (CP/MAS) ^{31}P NMR spectra. Thus all of the 1:1 complexes ($n = 1$) are shown to have the tetrameric cubane structure. The 2:1 complexes exist only for the L = DMPP case. The X = Cl complex has an ionic structure $[(DMPP)_4Cu]^+[CuCl_2]^-$, which represents a new structure type for adducts of copper(I) halides with neutral ligands. Halogen-bridged dimeric structures, $[(DMPP)_2CuX]_2$, are proposed for the 2:1 X = Br, I complexes. The 3:1 complexes have mononuclear $[L_3CuX]$ structures.

Introduction

Copper(I) displays a wide diversity in its structural chemistry, and this is well illustrated by the variety of structural types which are encountered in complexes of copper(I) halides. Neutral phosphine and amine ligands form mononuclear or multinuclear complexes with copper(I) halides in which the copper coordination number ranges from 2 to 4.[2-7] The greatest range of structural types has been found for the case of tertiary phosphine ligands, of which the most extensively studied is triphenylphosphine, Ph_3P.[2-6] Phospholes, such as 1-phenyl-3,4-dimethylphosphole (DMPP)[8-12] and 1-phenyldibenzophosphole (DBP),[13,14] are phosphorus donor ligands with unusual donor properties.[9-13] We have recently reported a study of the complexes of these two phosphole ligands with gold(I) halides, which showed that these ligands have significantly different coordination properties compared with those of PPh_3.[15] As part of a continuing program of investigation of the structures and properties of transition-metal phosphole complexes,[9,10,13,14,16-19] we now report the results of a study of a number of copper(I) halide complexes with the phospholes DMPP and DBP. The only phosphole complexes of copper which have been reported to date[20] are $[(DBP)_3Cu(BH_3CN)]$ and $[(DBP)_2CuBH_4]$, and no such complexes with copper(I) halides have yet been reported. Vibrational spectroscopy has proved to be a useful technique for the structural determination of copper(I) halide complexes, and data for most of the structural types encountered in complexes of tertiary phosphines are now available.[7,28-36] More recently, the technique of cross-polarization


DMPP


DBP

---

(1) (a) University of Nevada. (b) University of Auckland. (c) University of Warwick. (d) Colorado State University. (e) JEOL NMR Applications Laboratory.

(2) Hathaway, B. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Vol. 5, p 533.

(3) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.

(4) McAuliffe, C. A. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979.

(5) Gill, J. T.; Mayerle, P. S.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 1155.

(6) Healy, P. C.; Pakawatchai, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1905.

(7) Bowmaker, G. A.; Cotton, J. D.; Healy, P. C.; Kildea, J. D.; Silong, S. D.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1989**, *28*, 1462.

(8) Mathey, F. *Top. Phosphorus Chem.* **1980**, *10*, 1.

(9) Mathey, F.; Fischer, J.; Nelson, J. H. *Struct. Bonding (Berlin)* **1983**, *55*, 153.

(10) Nelson, J. H.; Mathey, F. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; pp 665–694.

(11) Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

(12) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275.

(13) Affandi, S.; Nelson, J. H.; Alcock, N. W.; Howarth, O. W.; Alyea, E. C.; Sheldrick, G. M. *Organometallics* **1988**, *7*, 1724 and references therein.

(14) Alea, E. C.; Malito, J.; Nelson, J. H. *Inorg. Chem.* **1987**, *26*, 4294.

(15) Attar, S.; Bearden, W. H.; Alcock, N. W.; Alea, E. C.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 425.

(16) Affandi, S.; Green, R. L.; Hsieh, B. T.; Holt, M. S.; Nelson, J. H.; Alyea, E. C. *Synth. React. Inorg. Met.—Org. Chem.* **1987**, *17*, 307.

(17) Nelson, J. H.; Affandi, S.; Gray, G. A.; Alyea, E. C. *Magn. Reson. Chem.* **1987**, *25*, 774.

(18) Vac, R.; Nelson, J. H.; Milosavljević, E. B.; Solujić, L. *Inorg. Chem.* **1989**, *28*, 3831.

(19) Gray, G. A.; Nelson, J. H. *Org. Magn. Reson.* **1980**, *14*, 14.

(20) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Wright, K. *Can. J. Chem.* **1974**, *52*, 2990.

(21) Bowmaker, G. A. *Adv. Spectrosc.* **1987**, *14*, 1.

(22) Bowmaker, G. A.; Healy, P. C. *Spectrochim. Acta* **1988**, *44A*, 115.

(23) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. *Spectrochim. Acta* **1988**, *44A*, 1219.

(24) Teo, B. K.; Barnes, D. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 681.

(25) Bowmaker, G. A.; Knappstein, R. J.; Tham, S. F. *Aust. J. Chem.* **1978**, *31*, 2137.

(26) Edwards, D. A.; Richards, R. *Spectrochim. Acta* **1978**, *34A*, 167.

(27) Bowmaker, G. A.; Rogers, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1249.

(28) Bowmaker, G. A.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1089.

(29) Bowmaker, G. A.; Engelhardt, L. M.; Healy, P. C.; Kildea, J. D.; Papasergio, R. I.; White, A. H. *Inorg. Chem.* **1987**, *26*, 3533.

(30) Menger, E. M.; Veeman, W. S. *J. Magn. Reson.* **1982**, *46*, 257.

(31) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Inorg. Chem.* **1984**, *23*, 3766.

(32) Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 831.

(33) Barron, P. F.; Dyason, J. C.; Healy, P. C.; Engelhardt, L. M.; Pakawatchai, C.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1099.

(34) Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 261.

0020-1669/91/1330-4743$02.50/0

magic-angle-spinning (CP/MAS) ^{31}P NMR spectroscopy has been shown to yield useful information about the structure and bonding in solid copper(I) complexes with phosphine ligands.[7,26-34] In many cases, these two techniques have been applied to complexes whose structures had already been established by X-ray crystallography. The present study provides an opportunity to investigate the use of a combination of these two methods to determine the structures of a complete set of new complexes. This approach is particularly appropriate for the series of complexes under study, as it proved to be difficult to obtain crystals which were suitable for X-ray diffraction studies. We have been able to obtain structural information with a high degree of reliability for most of the new complexes, and the results are in agreement with the structure determined by X-ray crystallography for the one compound giving suitable crystals.

Experimental Section

Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. When necessary, solvents were dried by standard procedures and stored over Linde 4-Å molecular sieves. All reactions involving phospholes were conducted under a dry N_2 atmosphere. Copper(I) chloride, bromide,[37] and iodide[38] were prepared by literature methods. 1-Phenyl-3,4-dimethylphosphole[39] (DMPP) and 1-phenyldibenzophosphole[16] (DBP) were prepared by literature methods.

Elemental analyses were performed by Galbraith laboratories, Knoxville, TN. Melting points were determined on a Meltemp apparatus and are uncorrected.

Far-infrared spectra were recorded at ambient temperature as polyethylene pellets on a Digilab FTS-60 Fourier transform infrared spectrometer employing a FTS-60V vacuum optical bench with a 6.25-μm Mylar film beam splitter, a mercury-lamp optical source, and a TGS detector. Solid-state cross-polarization magic-angle-spinning (CP/MAS)$^{31}P\{^1H\}$ NMR spectra were obtained on Nicolet NT-150 (^{31}P at 60.745 MHz) and JEOL GX-270 (^{31}P at 109.25 MHz) wide-bore spectrometers using 20- and 40-kHz sweep widths, recycle delay times of 1–6 s, and proton decoupling fields of 10 G. Between 200 and 300 mg of the compounds were spun at 3–4.5 kHz in Delrin or Kel-F rotors. The chemical shifts were referenced to 85% H_3PO_4 via an external sample of solid PPh_3 ($\delta = -6.0$ ppm). The uncertainties in chemical shifts are estimated to be ± 0.5 ppm.

Syntheses. [(phosphole)CuX]$_4$ Complexes. (a) [(DBP)CuCl]$_4$ and [(DBP)CuBr]$_4$. These two complexes were prepared by similar procedures except that ethanol was used as the solvent for the bromide. To a solution containing 0.41 g (2.41 mmol) of $CuCl_2 \cdot 2H_2O$ in 20 mL of acetone a solution of DBP (0.95 g, 3.65 mmol) in 30 of mL acetone was slowly added with constant stirring at ambient temperature. Over a 5-min period, the initially dark brown solution became colorless, and a colorless precipitate formed. The mixture was stirred magnetically for 2 h at ambient temperature, and the precipitate was isolated by filtration and vacuum-dried overnight.

(b) [(DBP)CuI]$_4$. A solution containing 0.62 g (3.26 mmol) of CuI and 0.86 g (3.29 mmol) of DBP in 400 mL benzene was refluxed overnight. The colorless solid which resulted was isolated by filtration and vacuum-dried overnight.

(c) [(DMPP)CuX]$_4$. These three complexes were all prepared in the same manner. Solutions containing 7.52 mmol of the appropriate copper(I) halide and 1.65 mL (8.77 mmol) of DMPP in 50 mL of CH_2Cl_2 were stirred magnetically at ambient temperature overnight. The yellow solutions were filtered to remove any unreacted CuX, and the volume of the filtrate was reduced to a few milliliters on a rotatory evaporator. Hexane was added, and the mixture was kept in a refrigerator at 5 °C overnight. The pale yellow microcrystals that formed were isolated by filtration, washed with hexane, and vacuum-dried overnight.

[(phosphole)$_2$CuX] Complexes. (d) Attempted Synthesis of [(DBP)$_2$CuX] Complexes. Solutions containing 4 mmol of CuX and 8 mmol of DBP in 500 mL of benzene were refluxed for 2 h, and the resulting colorless solutions were filtered. The volumes of the filtrates were reduced to a few milliliters on a rotatory evaporator, and hexane was added. The colorless precipitates that formed were shown to be [(DBP)$_3$CuX] by elemental analyses and far-infrared spectroscopy. Similarly, solutions containing 10 mmol of DBP and 5 mmol of CuX in $CHCl_3$ were stirred magnetically for 2 h. The colorless precipitates that formed were isolated by filtration and shown to be [(DBP)CuX]$_4$. Addition of diethyl ether to the filtrates caused precipitation of [(DBP)$_3$CuX]. These complexes were isolated with yields which suggest that the following reaction occurs:

$$8CuX + 16DBP \rightarrow [(DBP)CuX]_4 + 4[(DBP)_3CuX] \quad (1)$$

Table I. Elemental Analyses and Melting Point Data for the (phosphole)$_n$CuX Complexes

complex	mp, °C	% C calcd	% C found	% H calcd	% H found	% yield
$[(DBP)CuCl]_4$	204–208	60.17	60.04	3.65	3.90	75
$[(DBP)CuBr]_4$	264–266	53.55	53.83	3.25	3.37	97
$[(DBP)CuI]_4 \cdot 0.5H_2O$[a]	295–298	47.02	47.08	3.07	2.97	68
$[(DMPP)CuCl]_4$[b]	115–119	50.18	50.17	4.57	4.71	81
$[(DMPP)CuBr]_4$	129–132	43.45	43.71	3.96	4.24	78
$[(DMPP)CuI]_4$[c]	142–144	38.06	38.68	3.47	3.42	85
$[(DMPP)_2CuCl]_2 \cdot 0.1CH_2Cl_2$[d,e]	104–108	59.81	59.75	5.47	5.70	67
$[(DMPP)_2CuBr]_2 \cdot 0.3CH_2Cl_2$[d]	93–96	53.51	53.52	4.93	4.98	69
$[(DMPP)_2CuI]_2 \cdot 0.2CH_2Cl_2$[d]	140–142	49.78	49.60	4.57	4.77	63
$[(DBP)_3CuCl]$	264–267	73.71	73.64	4.48	4.63	90
$[(DBP)_3CuBr]$	258–261	70.17	70.14	4.26	4.47	76
$[(DBP)_3CuI] \cdot 1.4C_6H_6$	243–245	69.35	69.07	4.43	4.70	80
$[(DMPP)_3CuCl] \cdot 0.2CH_2Cl_2$[d,f]	144–146	63.87	64.08	5.84	5.90	61
$[(DMPP)_3CuBr] \cdot 0.4CH_2Cl_2$[d]	148–150	58.91	58.97	5.42	5.54	75
$[(DMPP)_3CuI]$	148–150	57.26	57.04	5.22	5.38	42

[a] The presence of H_2O was confirmed by the observation of a broad IR band at 3604 cm^{-1} due to ν_{O-H}, recorded as a Nujol mull between KBr plates. [b] % Cl: calcd, 12.35; found, 12.28. [c] % I: calcd, 33.52; found, 33.57. [d] The presence of CH_2Cl_2 was confirmed by ^1H NMR, $\delta = 5.3$ ppm (singlet). [e] % Cl: calcd, 8.79; found, 8.63. [f] % Cl: calcd, 7.30; found, 7.16.

(e) [(DMPP)$_2$CuX]. These three compounds were prepared in the same manner as the [(DMPP)CuX]$_4$ complexes, except that the DMPP/CuX molar ratios were 2.

[(phosphole)$_3$CuX] Complexes. (f) [(DBP)$_3$CuCl] and [(DBP)$_3$CuBr]. These two complexes were prepared by the reduction of CuX_2 with DBP in acetone. A solution containing 0.40 g (2.36 mmol) of $CuCl_2 \cdot 2H_2O$ and 2.17 g (8.33 mmol) of DBP in 100 mL of acetone was stirred magnetically at ambient temperature for 2 h. The resulting colorless precipitate was isolated by filtration and vacuum dried overnight.

(g) [(DBP)$_3$CuI]. A solution containing 0.75 g (3.96 mmol) of CuI and 3.25 g (12.47 mmol) of DBP in 200 mL of benzene was refluxed overnight. The solution was filtered, the volume of the filtrate was reduced to a few milliliters on a rotary evaporator, and *n*-hexane was added. The mixture was placed in a refrigerator at 5 °C overnight. The precipitate that formed was isolated by filtration and vacuum-dried overnight.

(h) [(DMPP)$_3$CuX]. These three compounds were prepared in the same manner as the [(DMPP)CuX]$_4$ complexes, except that the DMPP/CuX molar ratios were 3.

(i) [(DMPP)$_4$Cu]ClO$_4$. Safety Note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these samples should be handled with great caution. A solution containing 0.615 g (1.88 mmol) of $[(CH_3CN)_4Cu]ClO_4$[40] and 1.42 mL (7.52 mmol) of DMPP in 100 mL of CH_2Cl_2 was stirred using a magnetic stirring bar at ambient temperature for 2 h and filtered, the volume of the filtrate was reduced to a few milliliters, and ethanol was added. The oil that formed was isolated by decantation and washed with hexane. A solution of this oil in $CDCl_3$ showed very broad ^{31}P and ^{63}Cu[41] NMR resonances which remained broad at 200 K. These resonances are probably broadened by the combined effects of paramagnetic copper(II) impurities and rapid ligand exchange.

---

(35) Bowmaker, G. A.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2825.

(36) Bowmaker, G. A.; Camus, A.; Healy, P. C.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1989**, *28*, 3883.

(37) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(38) (a) Kaufman, G. B.; Pinnell, R. P. *Inorg. Synth.* **1960**, *6*, 3. (b) Kaufman, G. B. *Inorg. Synth.* **1968**, *11*, 215.

(39) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

(40) $[(CH_3CN)_4Cu]ClO_4$ was prepared by boiling copper powder with $[Cu(H_2O)_6](ClO_4)_2$ in CH_3CN containing a few drops of $HClO_4$. The complex crystallized upon cooling, and it was stored under an inert atmosphere. See Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2053.

(41) Hetherington, A.; Levason, W.; Spicer, M. D. *Polyhedron* **1990**, *9*, 1609.

Table II. Crystal and Refinement Data for $[(DMPP)CuI]_4$

fw	1514.6	d(calcd), g/cm^3	1.82
a, Å	21.058 (4)	linear abs coeff, cm^{-1}	38.7
b, Å	12.059 (2)	transm coeff	0.49–0.83
c, Å	23.425 (7)	temp, °C	20
β, deg	111.50 (2)	λ, Å	0.710 69
space group	$C2/c$	final $R(F)^a$	0.037
V, Å^3	5542 (2)	final $R_w(F)^b$	0.038
Z	4 (tetramers)		

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F) = [\sum w(|F_o| - |F_c|^2)/\sum w|F_o|^2]^{1/2}$; $w = (1/\sigma^2)(|F_o|)$.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for $[(DMPP)CuI]_4$

atom	x	y	z	U^a
Cu(1)	691.9 (5)	5866.3 (8)	8028.8 (4)	64 (1)
Cu(2)	−280.4 (6)	7521.0 (10)	7975.6 (4)	78 (1)
I(1)	−520.7 (3)	5335.3 (5)	8123.9 (2)	62 (1)
I (2)	1010.1 (3)	8003.9 (4)	8204.6 (2)	67 (1)
P(1)	1479.1 (10)	4945.2 (16)	8805.8 (8)	52 (1)
P(2)	−763.4 (11)	8479.2 (20)	8535.7 (10)	68 (1)
C(11)	1526 (4)	3449 (6)	8708 (3)	50 (3)
C(12)	2087 (4)	2843 (6)	9070 (4)	72 (4)
C(13)	2116 (6)	1724 (7)	8986 (4)	100 (5)
C(14)	1597 (5)	1193 (7)	8545 (4)	90 (5)
C(15)	1034 (5)	1772 (7)	8194 (4)	86 (4)
C(16)	1913 (4)	2885 (6)	8266 (3)	70 (4)
C(17)	1411 (4)	5144 (6)	9538 (3)	60 (3)
C(18)	1976 (4)	5622 (6)	9939 (3)	59 (3)
C(19)	2059 (5)	6001 (7)	10575 (3)	84 (4)
C(110)	2520 (4)	5734 (5)	9694 (3)	56 (3)
C(111)	3207 (4)	6163 (7)	10079 (4)	79 (4)
C(112)	2347 (4)	5394 (5)	9116 (3)	56 (3)
C(21)	−561 (4)	8036 (7)	9324 (4)	65 (4)
C(22)	−911 (5)	8421 (9)	9665 (4)	99 (5)
C(23)	−762 (5)	8097 (9)	10257 (5)	114 (6)
C(24)	−251 (5)	7329 (8)	10525 (4)	90 (5)
C(25)	110 (6)	6934 (9)	10189 (4)	111 (5)
C(26)	−44 (4)	7288 (8)	9600 (4)	88 (4)
C(27)	−733 (4)	9948 (7)	8544 (4)	75 (4)
C(28)	−1355 (5)	10369 (7)	8225 (4)	82 (4)
C(29)	−1520 (7)	11587 (8)	8127 (5)	132 (7)
C(210)	−1887 (4)	9529 (8)	7990 (3)	84 (4)
C(2111)	−2595 (5)	9818 (11)	7567 (5)	131 (6)
C(212)	−1664 (4)	8501 (8)	8160 (3)	80 (4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Structural Parameters for $[(DMPP)CuI]_4$

	Bond Angles (deg)		
Cu(2)–Cu(1)–I(1)	58.9	Cu(2)–Cu(1)–I(2)	57.4
I(1)–Cu(1)–I(2)	114.0	Cu(2)–Cu(1)–P(1)	133.6 (1)
I(1)–Cu(1)–P(1)	104.7 (1)	I(2)–Cu(1)–P(1)	106.5 (1)
Cu(2)–Cu(1)–Cu(1a)^a	103.7	P(1)–Cu(1)–Cu(1a)	148.8 (1)
I(2)–Cu(1)–Cu(2a)	56.9	P(1)–Cu(1)–Cu(2a)	152.6 (1)
Cu(1a)–Cu(1)–Cu(2a)	56.1	Cu(2)–Cu(1)–I(1a)	107.3
I(1)–Cu(1)–I(1a)	104.1	I(2)–Cu(1)–I(1a)	108.8
P(1)–Cu(1)–I(1a)	119.1 (1)	Cu(1a)–Cu(1)–I(1a)	56.3
Cu(2a)–Cu(1)–I(1a)	57.7	Cu(1)–Cu(2)–I(1)	58.6
Cu(1)–Cu(2)–I(2)	58.0	I(1)–Cu(2)–I(2)	114.4
Cu(1)–Cu(2)–P(2)	144.2 (1)	I(1)–Cu(2)–P(2)	106.1 (1)
I(2)–Cu(2)–P(2)	114.9	Cu(1)–Cu(2)–Cu(1a)	63.7
I(1)–Cu(2)–Cu(1a)	55.7	I(2)–Cu(2)–Cu(1a)	106.9
P(2)–Cu(2)–Cu(1a)	138.2 (1)	Cu(1)–Cu(2)–Cu(2a)	62.5
I(1)–Cu(2)–Cu(2a)	104.3	I(2)–Cu(2)–Cu(2a)	58.1
P(2)–Cu(2)–Cu(2a)	148.5 (1)	Cu(1a)–Cu(2)–Cu(2a)	57.9
Cu(1)–Cu(2)–I(2a)	109.3	I(1)–Cu(2a)–I(2a)	106.1
I(2)–Cu(2)–I(2a)	108.7	P(2)–Cu(2)–I(2a)	106.1
Cu(1a)–Cu(2)–I(2a)	55.8	Cu(2a)–Cu(2)–I(2a)	56.4
Cu(1)–I(1)–Cu(2)	62.5	Cu(1)–I(1)–Cu(1a)	69.1
Cu(2)–I(1)–Cu(1a)	66.6	Cu(1)–I(2)–Cu(2)	64.6
Cu(1)–I(2)–Cu(2a)	67.3	Cu(2)–I(2)–Cu(2a)	65.4
Cu(1)–P(1)–C(11)	116.3 (2)	Cu(1)–P(1)–C(17)	114.5 (3)
Cu(2)–P(2)–C(21)	117.0 (3)	Cu(2)–P(2)–C(27)	119.8 (4)
	Bond Lengths (Å)		
Cu(1)–Cu(2)	2.831 (2)	Cu(1)–I(1)	2.723 (1)
Cu(1)–I(2)	2.657 (1)	Cu(1)–P(1)	2.255 (2)
Cu(1)–Cu(1a)	3.059 (2)	Cu(1)–Cu(2a)	2.962 (1)
Cu(1)–I(1a)	2.668 (1)	Cu(2)–I(1)	2.730 (1)
Cu(2)–I(2)	2.638 (1)	Cu(2)–P(2)	2.252 (3)
Cu(2)–Cu(1a)	2.962 (1)	Cu(2)–Cu(2a)	2.880 (3)
Cu(2)–I(2a)	2.689 (1)	I(1)–Cu(1a)	2.668 (1)
I(2)–Cu(2a)	2.689 (1)		

[a] Refers to atoms that are related by summetry; i.e., 1a = 1′.

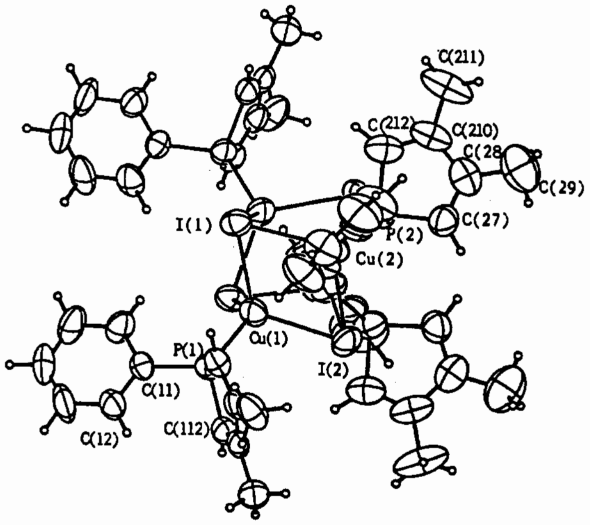


Figure 1. Structure of $[(DMPP)CuI]_4$. The 50% thermal ellipsoids are shown. Hydrogen atoms have an arbitrary radius of 0.12 Å.

The elemental analyses, melting points, and yields of the complexes prepared are given in Table I.

X-ray Crystal Structure Determination. Transparent yellow plates of tetrakis(μ_3-iodo)tetrakis(1-phenyl-3,4-dimethylphosphole)tetracopper(I) were isolated from a CH_2Cl_2/Et_2O solution. Crystal data and additional details of data collection and refinement are given in Table II. Intensity data were taken with a Syntex P2$_1$ four-circle diffractometer in the ω–2θ scan mode and were corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method. Systematic absences (hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$) indicated the space groups $C2/c$ or Cc; the former was initially examined and shown to be correct by successful refinement. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.07$ Å^2, and were inserted at calculated positions and not refined. Final refinement was by cascaded least-squares methods (minimizing $\sum w(F_0 - F_c)^2$). The largest positive and negative peaks on final difference Fourier syntheses were of height (e/Å^3) ±0.5. Weighting schemes of the form $1/(\sigma^2(F) + gF^2)$ were shown to be satisfactory by weight analysis. Three standard reflections monitored every 200 reflections showed no change. Computing was done with the SHEXTL system[42] on a Data General DG 30 computer. Scattering factors were taken from ref 43. Final atom coordinates are given in Table III, and selected bond lengths and angles, in Table IV.

Results and Discussion

The phosphole ligands 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP) were reacted with the copper(I) halides CuX (X = Cl, Br, I) in mole ratios of n:1 (n = 1–4). No complexes of 4:1 stoichiometry were obtained with either ligand, and this parallels the behavior of tertiary arylphosphines such as PPh_3, but contrasts with the situation for PMe_3, where the existence of the 4:1 adducts has been established.[41,44,45] In the case of DMPP, complexes with n = 1, 2, and 3 were isolated,

---

(42) Sheldrick, G. M. *SHEXTL User Manual*; Nicolet: Madison, WI, 1981.

(43) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(44) Schmidbaur, H.; Adlkofer, J.; Schwirten, K. *Chem. Ber.* **1972**, *105*, 3382.

(45) Bowmaker, G. A.; Healy, P. C.; Engelhardt, L. M.; Kildea, J. D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 1697.

Table V. Cubane Complexes of the Type $[(R_3P)CuX]_4$ and Some of Their Structural Parameters

		dist,[a] Å				angle,[a] deg			
complexes	cryst sym	Cu–P	Cu–X	Cu···Cu	X···X	Cu–X–Cu	X–Cu–X	P–Cu–X	ref
$[(Ph_3P)CuCl]_4$	C_2	2.192	2.444	3.307	3.501	84.95	95.02	121.90	49
$[(Ph_3P)CuBr]_4$	C_2	2.207	2.555	3.087	3.810	81.40	97.89	119.50	31
$[(Ph_3P)CuI]_4$	C_1	2.254	2.692	3.019	4.365	69.76	109.0	111.70	32
$[(Et_3P)CuCl]_4$	T_d	2.176	2.438	3.211	3.657	82.36	97.15	120.02	51
$[(Et_3P)CuBr]_4$	T_d	2.199	2.544	3.184	3.932	77.48	101.25	116.80	51
$[(Et_3P)CuI]_4$	T_d	2.254	2.684	2.927	4.380	66.10	109.38	109.56	50
$[(t\text{-}Bu_3P)CuBr]_4$	C_3	2.228	2.587	3.485	3.832	84.40	95.22	121.63	53
$[(MePh_2P)CuI]_4$	C_2	2.250	2.689	2.930	4.406	67.75	109.52	109.22	52
$[(DMPP)CuI]_4$	C_2	2.253	2.684	2.933		65.92	109.35	109.55	*b*

[a] Average values. [b] From this work.

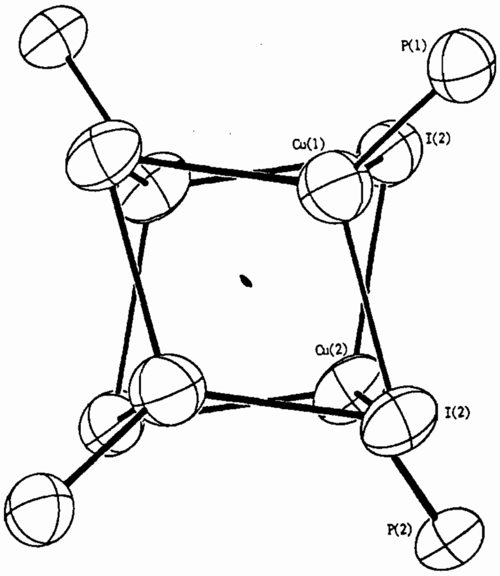
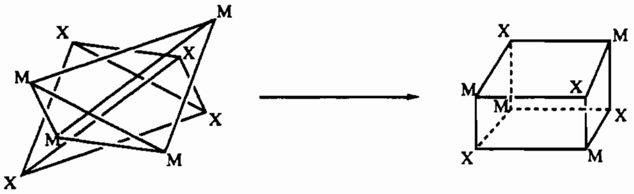


Figure 2. Projection of the $P_4Cu_4I_4$ core of the $[(DMPP)CuI]_4$ molecule, viewed down the unique C_2 axis, illustrating the distortion of the cubane structure. C and H atoms have been omitted for clarity.

whereas with DBP only the $n = 1$ and $n = 3$ compounds were obtained. Reaction mixtures containing a 2:1 DBP:CuX ratio yielded mixtures of the 1:1 and 3:1 complexes. Neither of the ligands yielded 3:2 complexes, a stoichiometry which has been found for PPh_3 complexes of the copper(I) halides.[5,46,47]

Crystal Structure of $[(DMPP)CuI]_4$. The crystal structure of the 1:1 complex of DMPP with CuI shows that this complex crystallizes as a tetramer, $[(DMPP)CuI]_4$, with the cubane structure which has previously been observed for 1:1 complexes of PPh_3 and other phosphine and amine ligands with copper(I) halides.[31,32,48–53] The structure of the molecule is shown in Figures 1 and 2. In this structure each of the four copper atoms is tetracoordinated through bonds to the P atom of the phosphole ligand and the three bridging iodine atoms, which are in turn tricoordinated. The important structural parameters for the complex are compared in Table V with those of other $[LCuX]_4$ complexes (L = tertiary phosphine ligand) with the cubane structure.

The parent molecule from which this type of complex derives is the hydrocarbon cubane, C_8H_8, a molecule which consists of a cube of carbon atoms enclosed within a cube of hydrogen atoms with a carbon on each corner to which a hydrogen atom is attached.[54] The polyhedron of cubane has full O_h symmetry. However, in the case of the M_4X_4 structure which contains atoms of two different elements at alternate corners of the cube, the highest symmetry which can be achieved is T_d. The alternate arrangement of M and X atoms in the cubane structure can be thought of as deriving from two interpenetrating M_4 and X_4 tetrahedra:[54]



The two tetrahedra need not be of the same size to preserve T_d symmetry, but only when they have this equivalence will the angles M–X–M = X–M–X = 90°, and the cubane will have planar faces. Thus, the relative magnitudes of these two angles give a clear indication of the degree to which the structure departs from that of an ideal cube due to the different sizes of the M_4 and X_4 tetrahedra. This may arise because of the different atomic radii of M and X and/or because of particular nonbonding (attractive or repulsive) interactions among the ligands attached to the M atom.

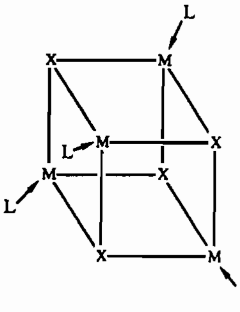
The results in Table IV show that both the Cu–I–Cu and the I–Cu–I angles vary appreciably and are quite different from the idealized values of 90°. The Cu–I–Cu angles range from Cu(1)–I(1)–Cu(2) = 62.5° to Cu(1)–I(1)–Cu(1′) = 69.1°. The average of the six independent values is 66 ± 2°, with the average for the angles involving I(1) (66.1°) being about the same as that for the angles involving I(2) (65.8°). For the I–Cu–I angles the range is from I(1)–Cu(1)–I(1′) = 104.1° to I(1)–Cu(2)–I(2) = 114.4°. The average of the six independent values is 109 ± 4°, with the average for the angles involving Cu(1) (109.0°) being about the same as that for the angles involving Cu(2) (109.7°). The irregularity in the interatomic angles is also reflected in the P–Cu–I angles. These range from P(1)–Cu(1)–I(1) = 104.7° to P(1)–Cu(1)–I(1′) = 119.0°. The average of the six independent values is 109 ± 6°. The irregularity in this and the other bond angles referred to above is due to a further reduction in symmetry from T_d for the isolated Cu_4I_4 cubane structure to C_2 in the crystal. The effect of the nature of the ligand L on the bonding in cubane $[LCuX]_4$ complexes can be seen by comparing the structures of complexes with different L and the same X. Thus, for example, for the series of complexes $[LCuBr]_4$ (L = Et_3P, Ph_3P, Bu^t_3P) there is a monotonic increase in the Cu–Br bond length and the Cu–Br–Cu bond angle. One factor which is no doubt important in this connection is the steric bulk of the ligand. A measure of this property is the ligand cone angle, which increases in the order Et_3P (132°) < Ph_3P (145°) < Bu^t_3P (182°).[55] In this connection, it can be noted that for the series $[LCuI]_4$ (L = DMPP, Et_3P, Ph_2MeP, Ph_3P) the Cu–I bond length and the Cu–I–Cu bond

---

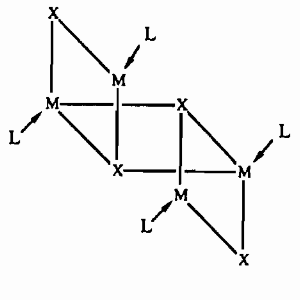
(46) Eller, P. G.; Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 2454.
(47) Dyason, J. C.; Engelhardt, L. M.; Pakawatchai, C.; Healy, P. C.; White, A. H. *Aust. J. Chem.* **1985**, *38*, 1243.
(48) Churchill, M. R.; Kalra, K. L. *J. Am. Chem. Soc.* **1973**, *95*, 5772.
(49) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065.
(50) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899.
(51) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2041.
(52) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267.
(53) Goel, R. G.; Beauchamp, A. L. *Inorg. Chem.* **1983**, *22*, 395.
(54) Johnson, B. F. G. *Transition Metal Clusters*; John Wiley and Sons: New York, 1980; Chapter 4.
(55) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

angle also show a monotonic increase, although the values of these parameters for the first three members of this series are very similar. This is an indication of the close similarity in the steric properties of DMPP to those of Et_3P (cone angle 132°) and Ph_2MeP (127°). Thus the effective cone angle for DMPP would appear to be about 130°.

Another possible structure for tetrameric $[LCuX]_4$ complexes is the so-called "step" structure which has been observed for the X = Br, I complexes with L = PPh_3.[47,56,57] The two main differences between this and the cubane structure are as follows: (1) There are both three- and four-coordinate copper atoms in the step isomer, whereas the cubane isomer contains only four-coordinate copper atoms. (2) Whereas all of the X atoms are triply bridging in the cubane isomer, the step isomer contains both doubly and triply bridging halogen atoms. It was originally postulated that the formation of the step isomer was favored by ligands with greater steric bulk,[58-60] and this, together with the conclusion reached above about the relatively low steric bulk of the DMPP ligand, would be consistent with the observed formation of the cubane isomer for $[(DMPP)CuI]_4$. However, the fact that cubane structures have been observed with the sterically very bulky $\mathrm{Bu^t{}_3P}$ ligand[53] tends to negate the above argument and indicates that the factors which determine the formation of the cubane or step structures are not well understood.



cubane



step structure

With still bulkier ligands than the ones mentioned above, structures of lower molecularity can occur. Thus, the complex $[(Cy_3P)CuCl]_2$ (Cy_3P = tricyclohexylphosphine) has a halogen-bridged dimer structure,[61,62] and $[(mes_3P)CuBr]$ (mes_3P = trimesitylphosphine is monomeric with nearly linear two-coordinated copper.[63] Clearly, since DMPP is at the low end of the scale of steric bulkiness, monomeric or dimeric structures would not be expected for its CuX complexes. Thus, the observation of a tetrameric structure in the present study is entirely in line with the structures of related complexes which are known to date.

Infrared Spectra. The far-infrared spectra of representative members of the $(DMPP)_nCuX$ series of complexes are shown in Figure 3, and the bands assigned to the copper-halogen vibrational frequencies are labeled. The basis of the assignments of the ν(CuX) bands is illustrated for the n = 3 series, where the wavenumbers of these bands show the normal decrease from X = Cl to Br. The ν(CuX) wavenumbers for all of the complexes studied are listed in Table VI, where they are compared with those of related PPh_3 complexes. The interpretation of the observed wavenumbers in terms of the structures of the complexes concerned is most straightforward for the 3:1 cases. For these complexes the ν(CuX) wavenumbers are close to those of the corresponding PPh_3 compounds,[23] which have been shown by X-ray crystallography to contain the four-coordinate mononuclear $[(PPh_3)_3CuX]$ species.[5,33] On the basis of this close correspondence in the ν(CuX) wavenumbers, analogous structures are proposed for the corresponding DMPP and DBP complexes. The 1:1 complexes of PPh_3 with copper(I) halides are tetramers with either the step[47,56,57] or the cubane structure[31,32,49] (vide supra). It has been shown that these two structures can be distinguished on the basis of the pattern of bands arising from vibrations of the Cu_4X_4 core in their far-IR spectra.[23-25] Comparison of the ν(CuX) wavenumbers obtained for the 1:1 DMPP and DBP complexes with those for the PPh_3 complexes (Table VI) indicates that they all have the cubane

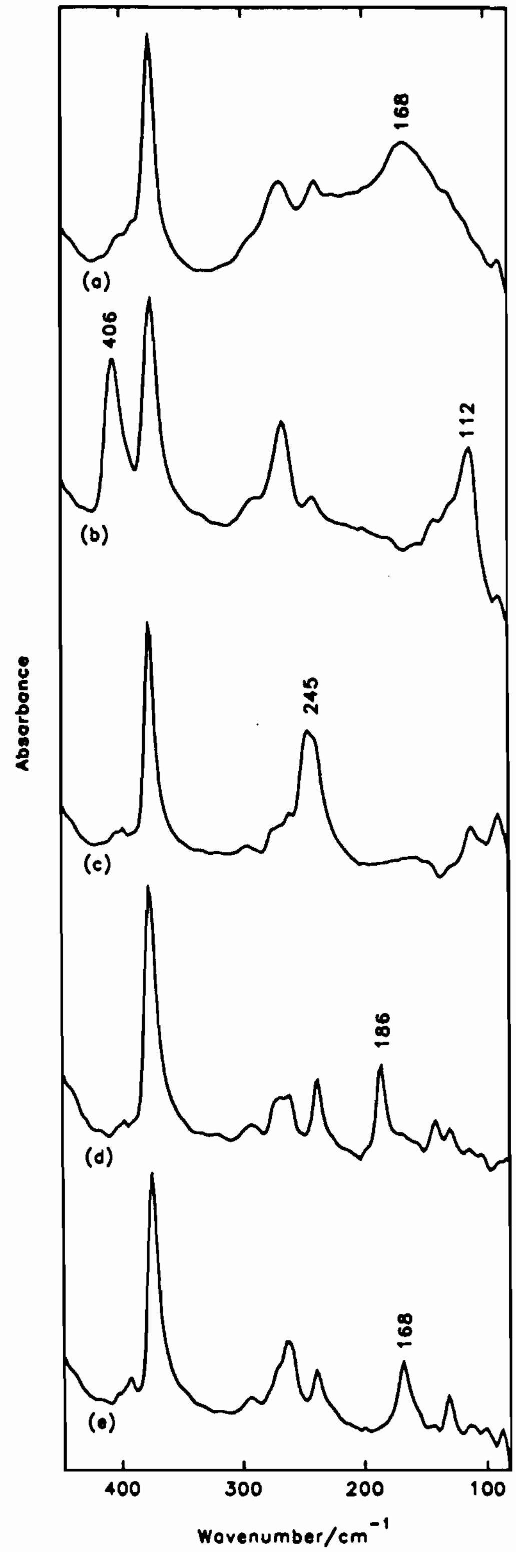


Figure 3. Far-infrared spectra of (a) (DMPP)CuCl, (b) $(DMPP)_2CuCl$, (c) $(DMPP)_3CuCl$, (d) $(DMPP)_3CuBr$, and (e) $(DMPP)_3$ CuI. The bands due to copper–halogen vibrations are labeled with their wavenumber.

---

(56) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.
(57) Churchill, M. R.; DeBoer, B. G.; Donovan, D. J. *Inorg. Chem.* **1975**, *14*, 617.
(58) Teo, B.-K.; Calabrese, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1256; *Inorg. Chem.* **1976**, *15*, 2467.
(59) Teo, B.-K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 185.
(60) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.
(61) Moers, F. G.; Op Het Veld, P. H. J. *Inorg. Nucl. Chem.* **1970**, *32*, 3225.
(62) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1979**, *18*, 166.
(63) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Inorg. Chem.* **1985**, *24*, 3719.

Table VI. Copper–Halogen Vibrational Frequencies (cm^{-1}) for $[L_nCuX]_m$ Complexes

L	X	$[LCuX]_4$ step	$[LCuX]_4$ cubane	$[L_2CuX]$	$[L_{1.5}CuX]_2$	$[L_2CuX]_2$	$[L_3CuX]$
DBP	Cl		186, 159				235
	Br		145, 120				178
	I		135, 86				156
DMPP	Cl		168 (br)			406, 112[a]	245
	Br		152, 122			141, 132	186
	I		139, 92			133, 117	168
PPh_3[b]	Cl		181, 162	298	220, 179		214
	Br	174, 135	144, 119	218	180, 128		164
	I	162, 109	138, 99	184	163, 107		138

[a] Proposed structure $[L_4Cu]^+[CuCl_2]^-$; the observed bands are assigned as ν_3, ν_2 of the $[CuCl_2]^-$ ion (see text). [b] Data for PPh_3 complexes from refs 21–24.

structure. This conclusion has been confirmed by X-ray crystallography in the case of $[(DMPP)CuI]_4$ (vide supra). The step structure can be ruled out, since this results in significantly higher ν(CuX) wavenumbers in comparison with the cubane structure. Monomeric structures can also be ruled out for similar reasons; it has been shown that the ν(CuX) wavenumbers for monomeric structures (which involve two-coordinate Cu) are much higher than those for the tetrameric structures (which involve three- and four-coordinate Cu).[7] No far-IR data have yet been reported for dimeric 1:1 complexes (which involve three-coordinate Cu). However, the ν(CuX) wavenumbers for such a structure would be expected to be at least as high as those for the binuclear $[(PPh_3)_{1.5}CuX]_2$ complexes (Table VI), which puts them well above the values observed for the 1:1 DMPP and DBP complexes. These complexes are thus all assigned the tetrameric cubane structure.

As noted above, DBP forms no complexes of 2:1 stoichiometry with copper(I) halides whereas DMPP forms 2:1 complexes with all three CuX (X = Cl, Br, I). In contrast with the situation for the 3:1 complexes, and also with that for the 2:1 complexes of PPh_3 with copper(I) halides,[27,28] the halogen-sensitive bands of the $(DMPP)_2CuX$ species do not exhibit a regularly decreasing trend in wavenumber from X = Cl to X = I. Thus $(DMPP)_2CuCl$ shows a strong band at 408 cm^{-1} (Figure 3) which has no counterpart in the spectra of any of the other DMPP complexes, and which therefore cannot be assigned as a vibration of coordinated DMPP. This band is higher in wavenumber than any yet assigned to a ν(CuCl) mode in a CuCl complex of a phosphine ligand (the highest value assigned to date is 355 cm^{-1} in a two-coordinate 1:1 complex)[7] and so is unlikely to arise from a species involving a PCuCl group in which the Cu atom is coordinated to DMPP. However, it is close to the wavenumber of the antisymmetric stretching mode ν_3 of the dichlorocuprate ion $[CuCl_2]^-$ (405 cm^{-1} in tri-*n*-butyl phosphate solution; 404–408 cm^{-1} in solid $[CuCl_2]^-$ salts).[64,65] Its assignment to this mode is confirmed by the observation of a strong band at 112 cm^{-1} (Figure 4) which is close to the wavenumber of the bending mode ν_2 of $[CuCl_2]^-$ (109 cm^{-1} in tri-*n*-butyl phosphate solution; 111 cm^{-1} in solid $[CuCl_2]^-$ salts).[64,65] This implies that the $(DMPP)_2CuCl$ complex is ionic in the solid state and can be formulated as $[(DMPP)_4Cu]^+[CuCl_2]^-$. This represents a new structure type for adducts of copper(I) halides with neutral ligands. The nearest examples of this type of behavior are the formation of ionic complexes $[(Me_3P)_4Cu]^+X^-$ in the 4:1 adducts of Me_3P with copper(I) halides,[44,45] and the $[(Me_3P)_4Cu]^+[CuMe_2]^-$ complex.[66] If the $(DMPP)_2CuBr$ complex had the same structure as the CuCl complex, it would show a strong IR band due to ν_3 of the dibromorocuprate ion $[CuBr_2]^-$ at about 320 cm^{-1} (322 cm^{-1} in tri-*n*-butyl phosphate solution; 314–321 cm^{-1} in solid $[CuBr_2]^-$ salts[64,65]). This is not the case, however, so this complex must have a different structure. The most obvious alternative is the mononuclear three-coordinate structure similar to that shown by

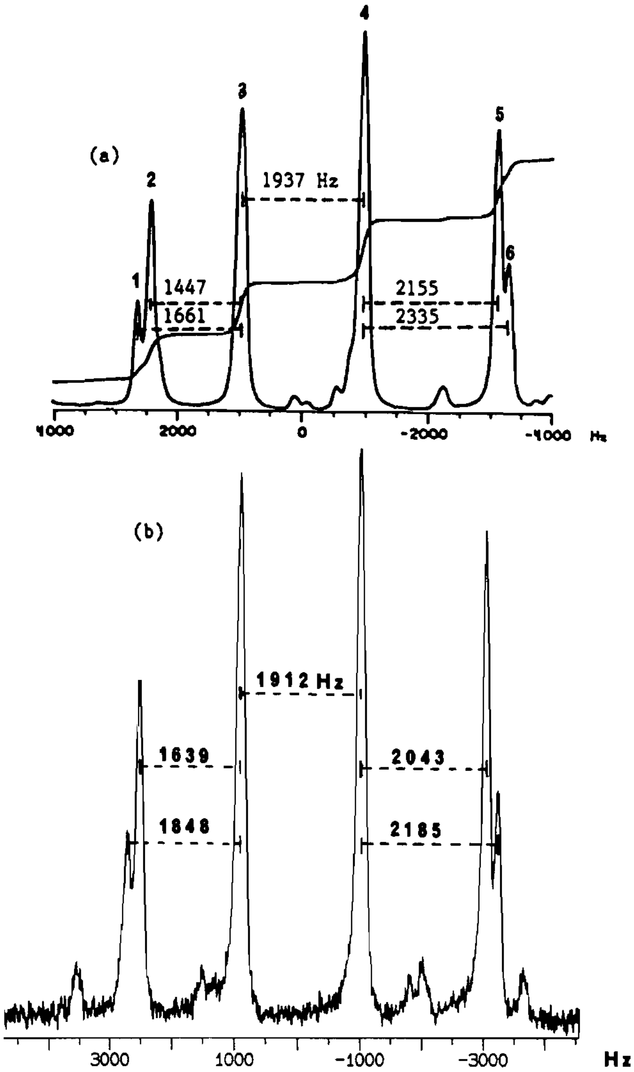


Figure 4. Comparison of the 60.75- (a) and 109.25-MHz (b) $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DBP)CuCl]_4$ showing the field dependence of the line splittings $\Delta\nu$.

the corresponding PPh_3 complex. Such a structure should give rise to a ν(CuBr) band at about 220 cm^{-1}, but this is also not observed experimentally. A third possible structure is the dimeric one $[(DMPP)_2CuBr]_2$ in which two Cu atoms are bridged by two Br atoms, and two phosphole ligands are terminally bound to each Cu atom to give a coordination number of four for each Cu. Such a structure has not been reported for PPh_3 complexes of the copper(I) halides, but has been observed for a 2:1 complex of PPh_2Me with CuI.[67] Unfortunately, no far-IR data have been reported for this compound. However, the 3:2 complexes of PPh_3

---

(64) Waters, D. N.; Basak, B. *J. Chem. Soc. A* **1971**, 2733.
(65) Bowmaker, G. A.; Brockliss, L. D.; Whiting, R. *Aust. J. Chem.* **1973**, *26*, 29.
(66) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208.
(67) Eller, P. G.; Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 2454.

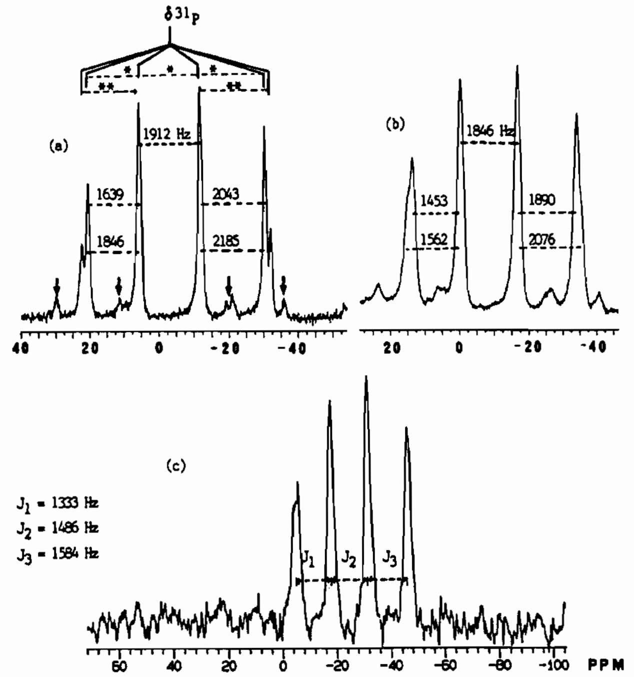


Figure 5. 109.25-MHz $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DBP)CuX]_4$ complexes: (a) X = Cl, ✱ = $J(^{63}Cu–P)$, ✱✱ = $J(^{65}Cu–P)$ (b) X = Br (c) X = I; ↓ = spinning sideband (SSB).

with copper(I) halides, $[(PPh_3)_{1.5}CuX]_2$, contain the same Cu_2X_2 unit in which the two Cu atoms are connected by two doubly bridging halogen atoms,[5,46,47] so that some idea of the expected positions of the $\nu(CuX)$ bands for the proposed dimer structure should be obtainable from the far-IR results for these species, which are given in Table VI. Thus $\nu(CuBr)$ should occur in the range 130–180 cm^{-1}. A partially resolved doublet at 141, 132 cm^{-1} occurs in this range in the infrared spectrum of the $(DMPP)_2CuBr$ complex, and a similar doublet occurs at 133, 117 cm^{-1} in the infrared spectrum of the $(DMPP)_2CuI$ complex. These bands are assigned as $\nu(CuX)$ of the Cu_2X_2 units in dimeric $[(DMPP)_2CuX]_2$ structures for the X = Br, I complexes. These conclusions are supported by the ^{31}P CP/MAS NMR results discussed below.

CP/MAS ^{31}P NMR Spectra. The CP/MAS ^{31}P NMR spectra for the 1:1 complexes are shown in Figures 4–6. They all contain asymmetric quartet splitting patterns of the type which has been reported previously for a range of copper(I) complexes with phosphine ligands.[7,28–36] This asymmetric splitting is due to the combined effects of scalar and dipolar spin–spin coupling between the phosphorus nucleus (^{31}P, nuclear spin = $^1/_2$) and the copper nucleus (^{63}Cu, ^{65}Cu, nuclear spin $I = {}^3/_2$) and the copper nuclear quadrupole coupling. This has been discussed previously by Menger and Veeman,[7] who presented calculations of the line positions for the components of the quartet in terms of the various coupling constants involved. These are the copper nuclear Zeeman interaction $\gamma_{Cu}\hbar B$, the copper nuclear quadrupole coupling constant e^2qQ, and the phosphorus–copper scalar and dipolar coupling constants a and $\mu_0\gamma_P\gamma_{Cu}\hbar^2/4\pi r^3$ (r = the Cu–P bond length). Menger and Veeman carried out their calculations for the case in which the ratio R of the dipolar to the scalar coupling constant (eq 2) is equal to 0.5 and calculated the quartet line positions as

$$R = \mu_0\gamma_P\gamma_{Cu}\hbar^2/4\pi a r^3 \qquad (2)$$

a function of the dimensionless parameter K (eq 3), which is

$$K = -3e^2qQ/4I(2I-1)\gamma_{Cu}\hbar B \qquad (3)$$

proportional to the ratio of the copper quadrupole coupling constant to the copper nuclear Zeeman term. From these calculated line positions the spacings $\Delta\nu_i$ (i = 1–3) between the adjacent lines in the quartet and the ratio of the two outermost spacings $\Delta\nu_3/\Delta\nu_1$ can be calculated as a function of K. The value of $\Delta\nu_3/\Delta\nu_1$ determined from an experimental spectrum can then be used to determine K, which can in turn be used to estimate the copper nuclear quadrupole coupling constant e^2qQ via eq 3.[7]

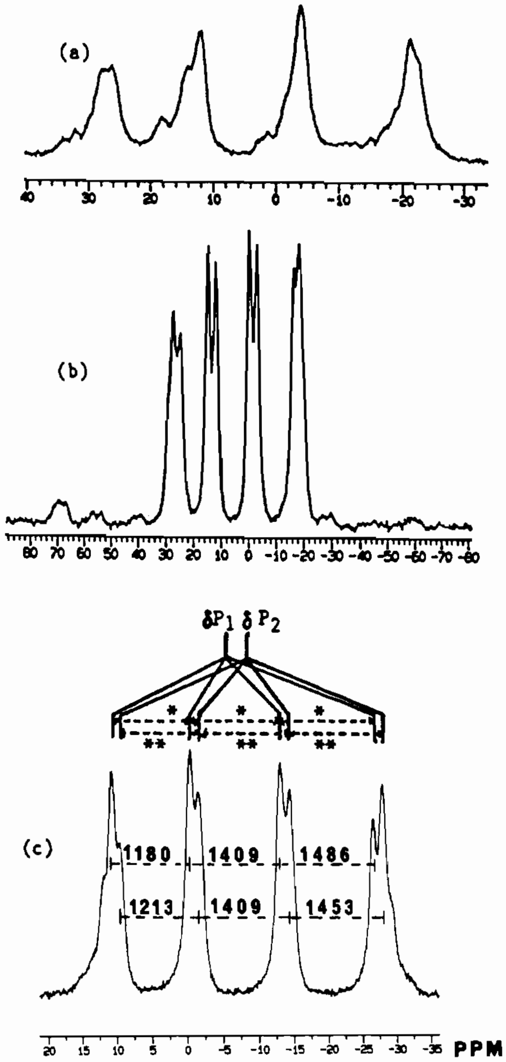


Figure 6. 109.25-MHz $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DMPP)CuX]_4$ complexes: (a) X = Cl; (b) X = Br; (c) X = I, ✱ = $J(^{63}Cu–P_1)$, ✱✱ = $J(^{63}Cu–P_2)$.

The line widths in the observed spectra vary considerably from one sample to another, the sharpest lines being obtained for the 1:1 DBPCuCl complex (Figure 4). In this case the lines are sufficiently narrow to allow resolution of the splittings arising from coupling of ^{31}P to ^{63}Cu (natural abundance 69.09%) and ^{65}Cu (30.91%) in the outermost lines in the quartet. Although this type of copper isotope splitting has been reported previously,[30] the resolution obtained in such spectra is not normally sufficient to allow its observation. That the splitting is due to coupling of the phosphorus nucleus to the two different isotopes of copper can be demonstrated by applying the method of analysis described above to the separate quartet splittings. This is a particularly favorable case to which to apply this method as there are no complications arising from separate signals from crystallographically inequivalent atoms, and the spectrum has been run at two different magnetic field strengths, corresponding to ^{31}P NMR frequencies of 60.75 and 109.25 MHz. The results of this analysis are given in Table VII. The expected relationships between the parameters determined for the two different copper isotopes and for the two different field strengths are as follows:

(a) The scalar coupling constant a for a particular copper isotope should be field independent, and the ratio $a(^{63}Cu)/a(^{65}Cu)$ should be equal to the ratio of the corresponding magnetogyric ratios $\gamma(^{63}Cu)/\gamma(^{65}Cu) = 0.933$.

(b) The nuclear quadrupole coupling constants e^2qQ for a particular copper isotope should be field independent, and the ratio

Table VII. Field Dependence of the CP/MAS ^{31}P NMR Splitting Parameters for $[(DBP)CuCl]_4$

	value determined at			
	60.75 MHz		109.25 MHz	
parameter	^{63}Cu	^{65}Cu	^{63}Cu	^{65}Cu
$\Delta\nu_1$, Hz	1447	1661	1639	1846
$\Delta\nu_2$, Hz	1937		1912	
$\Delta\nu_3$, Hz	2155	2335	2043	2185
a/h, Hz	1846	1978	1865	1981
$a(^{63}Cu)/a(^{65}Cu)$	0.933		0.941	
$\gamma(^{63}Cu)/\gamma(^{65}Cu)$	0.933			
$\Delta\nu_3/\Delta\nu_1$	1.489	1.406	1.246	1.184
K	0.127	0.110	0.073	0.057
B, T	3.523		6.342	
e^2qQ/h, MHz	20.22	18.76	20.92	17.44
$e^2qQ(^{63}Cu)/e^2qQ(^{65}Cu)$	1.08		1.20	
$Q(^{63}Cu)/Q(^{65}Cu)$	1.08			

Table VIII. CP/MAS ^{31}P NMR Parameters

	δ/ppm[a]		$\Delta\nu_i$/Hz[a]	
complex	A	B	A	B
$[(DBP)CuCl]_4$	−3.1	*b*	1639, 1912, 2043	*b*
$[(DBP)CuBr]_4$	−8.2	*b*	1453, 1846, 1890	*b*
$[(DBP)CuI]_4$	−24.8	*b*	1333, 1486, 1584	*b*
$[(DMPP)CuCl]_4$	6.2	4.0	1562, 1741, 2137	1565, 1741, 2068
$[(DMPP)CuBr]_4$	7.2	4.6	1390, 1649, 1776	1425, 1629, 1693
$[(DMPP)CuI]_4$	−6.4	−7.9	1180, 1409, 1486	1213, 1409, 1453
$[(DMPP)_2CuCl]_2$[c]	14.5	*b*	746, 756, 746	*b*
$[(DMPP)_2CuBr]_2$	9.1	2.9	912, 936, 1015	1126, 1161, 1268
$[(DMPP)_2CuI]_2$	4.7	2.4	805, 897, 995	1053, 1083, 1181
$[(DBP)_3CuCl]$	−1.1	*d*	*d*	*d*
$[(DBP)_3CuBr]$	−2.5	*d*	*d*	*d*
$[(DBP)_3CuI]$	−4.5	*d*	854, 897, 908	*b*
$[(DMPP)_3CuCl]$	2.0	*b*	874, 974, 788	*b*
$[(DMPP)_3CuBr]$	5.3	*b*	878, 869, 839	*b*
$[(DMPP)_3CuI]$	7.0	*d*	*d*	*d*

[a] Parameters are given for two separate quartets A (downfield) and B (upfield) where applicable. [b] Only one quartet was observed. [c] Proposed structure $[(DMPP)_4Cu]^+[CuCl_2]^-$; the observed signals are assigned to the $[(DMPP)_4Cu]^+$ ion. [d] Spectrum is too complex to analyze; the chemical shift for the center of the spectrum is given.

Table IX. Scalar Coupling Constants a/h and Nuclear Quadrupole Coupling Constants e^2qQ/h Obtained from CP/MAS ^{31}P NMR Spectra for $[LnCuX]_4$ Complexes

L	X	structure	a/h, Hz	$\Delta\nu_3/\Delta\nu_1$	K	e^2qQ/h, MHz	ratio[a]
DBP[b]	Cl	cubane	1865	1.25	0.073	21	
	Br	cubane	1730	1.30	0.086	25	
	I	cubane	1468	1.19	0.058	17	
DMPP[b]	Cl	cubane	1813	1.37	0.102	29	1.1
			1791	1.32	0.091	26	
	Br	cubane	1605	1.28	0.081	23	1.4
			1582	1.19	0.058	17	
	I	cubane	1358	1.26	0.076	22	1.3
PPh_3[c]	Cl	cubane	1358	1.20	0.061	17	
			1963	1.22	0.067	21	1.2
	Br	cubane	1943	1.28	0.082	26	
			1873	1.17	0.053	17	1.2
	Br	step	1877	1.20	0.061	20	
			1860	1.21	0.064	20	1.9
	I	cubane	1780	1.44	0.118	38	
			1557	1.19	0.059	19	1.1
	I	step	1527	1.17	0.054	17	
			1647	1.37	0.102	33	1.2
	I	step[d]	1660	1.29	0.084	27	
			1627	1.41	0.111	35	1.5
			1617	1.24	0.071	23	

[a] Ratio of larger to smaller nuclear quadrupole coupling constant for the cases where signals from two sites are observed. [b] Spectra obtained at a magnetic field strength of 6.342 T (^{31}P resonance frequency = 109.25 MHz). [c] Data from refs 31 and 32; spectra obtained at a magnetic field strength of 7.048 T (^{31}P resonance frequency = 121.47 MHz). [d] Desolvated complex.

$e^2qQ(^{63}Cu)/e^2qQ(^{65}Cu)$ should be equal to the ratio of the corresponding nuclear quadrupole moments $Q(^{63}Cu)/Q(^{65}Cu) = 1.08$.

These expectations are borne out well by the results; the only exception being the rather low value of $e^2qQ(^{65}Cu)$ determined from the 109.25-MHz spectrum.

The ^{31}P chemical shifts δ and the quartet splittings $\Delta\nu_i$ measured from the CP/MAS spectra are given in Table VIII. The results of the analysis of the splitting patterns for the $[LCuX]_4$ complexes (L = DBP, DMPP) are given in Table IX, where they are compared with those determined from the previously reported spectra of the corresponding triphenylphosphine complexes (L = PPh_3).[31,32] The accuracy of the results can be checked by making a comparison with the quadrupole coupling constant obtained from nuclear quadrupole resonance (NQR) spectroscopy for $[(PPh_3)CuCl]_4$,[68] which is the only case for which both CP/MAS and NQR data have been reported and for which the assumption of axial symmetry at the copper atom that is made in Menger and Veeman's analysis[30] is valid. For such a case, the nuclear quadrupole coupling constant is obtained from the NQR resonance frequency by multiplying by 2, yielding the values 26.0 and 27.5 MHz (two NQR frequencies are observed, due to the presence of two crystallographically inequivalent copper sites in the structure). The higher of the two values obtained from the CP/MAS spectrum (Table VII) is in good agreement with these, but the lower value is not, and the reason for this is not clear at present. This result clearly indicates that the nuclear quadrupole coupling constants obtained from the CP/MAS spectra are not very accurate. However, in order to investigate the structure information which may be contained in the asymmetry of the observed quartet splitting patterns, we have used this method to determine the values of these coupling constants for the compounds investigated in the present study. This is necessary because other more direct measures of this asymmetry cannot be directly compared in all cases. Thus, the difference $\Delta\nu_3 - \Delta\nu_1$ depends not only on the quadrupole coupling constant but also on the scalar coupling constant a. This dependence on a is eliminated if the ratio $\Delta\nu_3/\Delta\nu_1$ is used as a measure of the asymmetry, but this ratio depends on the magnetic field strength B at which the spectrum is obtained, as well as on the quadrupole coupling constant. Thus, only by calculating the actual values of the coupling constants is it possible to compare results for different compounds obtained at different field strengths.

We now consider what structural information can be deduced from the qudrupole coupling constants determined from the CP/MAS spectra of the DBP and DMPP complexes. In order to do this we look first at the results for the PPh_3 complexes, for which the structures are known. The cubane structures (Table IX) all have two coupling constants whose ratio is 1.2 or less. The step structures have two values whose ratio is 1.2 or greater. The ratio of 1.2 for the solvated form of step $[(PPh_3)CuI]_4$ is anomalously low; the other step structures show considerably larger ratios of 1.9 and 1.5, as would be expected for a structure which contains two Cu sites with different coordination environments (the coupling constant for the trigonal planar environment should be considerably larger than that for the tetrahedral environment).[21] The existence of this anomaly introduces some uncertainty into the assignment of structure on the basis of these ratios. In the case of the DBP complexes this is not a problem, as only one type of P and Cu atom is seen, and this is consistent only with the cubane structure. The coupling constants for $[(DMPP)CuX]_4$ are all significantly greater in magnitude (by about the same factor) compared with those for the corresponding cubane $[(PPh_3)CuX]_4$ complex. However, they are all sufficiently close to those of the cubane PPh_3 complexes that the cubane structure is indicated for these, as has been verified in the case of the iodide by an X-ray structure determination (vide supra). This is completely consistent with the far-IR data, as discussed above. The main additional result provided by the CP/MAS spectra is the fact that the DMPP complexes appear to be more distorted from ideal tetrahedral symmetry than the DBP complexes, as evidenced

---

(68) Okuda, T.; Hiura, M.; Yamada, K.; Negita, H. *Chem. Lett.* **1977**, 367.

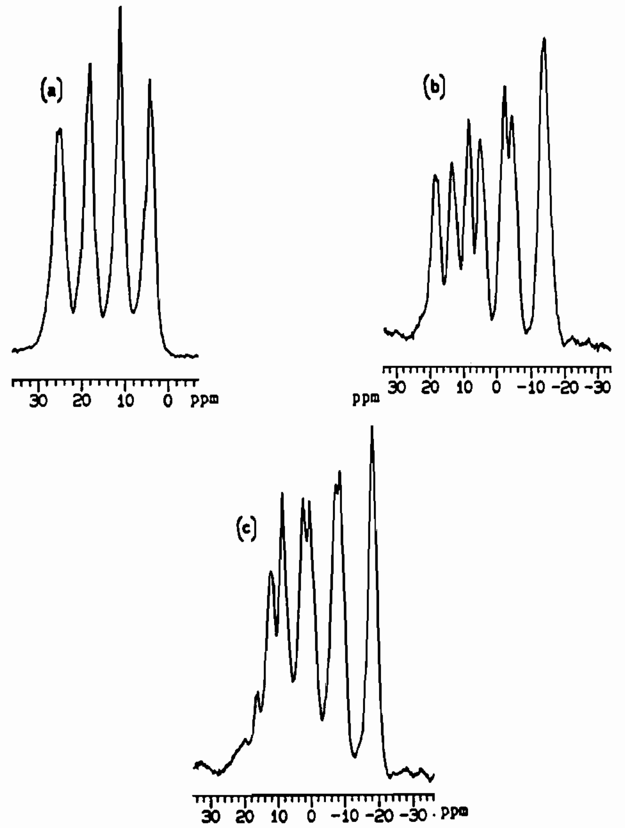


Figure 7. 109.25-MHz $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DMPP)_2CuX]$ complexes: (a) $[(DMPP)_4Cu][CuCl_2]\cdot 0.1CH_2Cl_2$; (b) $[(DMPP)_2CuBr]_2\cdot 0.6CH_2Cl_2$; (c) $[(DMPP)_2CuI]_2\cdot 2CH_2Cl_2$.

Table X. Scalar Coupling Constants a/h and Nuclear Quadrupole Coupling Constants e^2qQ/h Obtained from ^{31}P CP MAS NMR Spectra for $[L_2CuX]_n$

L	X	structure	a/h, Hz	$\Delta\nu_3/\Delta\nu_1$	K	e^2qQ/h, MHz
DMPP[a]	Cl	$[L_4Cu][CuCl_2]$	749	1.00	0.000	0
	Br	$[L_2CuBr]_2$	954	1.11	0.036	10
			1165	1.18	0.057	16
	I	$[L_2CuI]_2$	899	1.24	0.070	20
			1106	1.12	0.039	11
PPh_3[b]	Cl	trigonal monomer	1213	1.52	0.134	43
	Br	trigonal monomer	1200	1.64	0.155	49
$T_\alpha Ph_2P$[c]	I	trigonal monomer	1170	1.63	0.153	49
	Cl	trigonal monomer	1190	1.53	0.136	43
			1277	1.76	0.177	56
	Br	trigonal monomer	1183	1.37	0.103	33
			1297	1.48	0.126	40
	I	trigonal monomer	1307	1.29	0.085	27

[a] Spectra obtained at a magnetic field strength of 6.342 T (^{31}P resonance frequency = 109.25 MHz). [b] Data from ref 28. Spectra obtained at a magnetic field strength of 7.048 T (^{31}P resonance frequency = 121.47 MHz). [c] Data from ref 29. Spectra obtained at a magnetic field strength of 7.048 T (^{31}P resonance frequency = 121.47 MHz). $T_\alpha Ph_2P$ = (2-methylphenyl)diphenylphosphine.

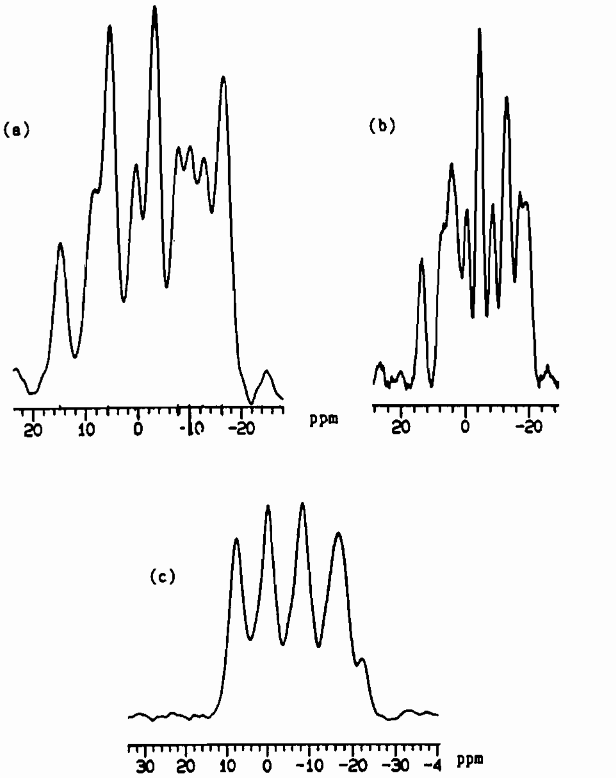


Figure 8. 109.25-MHz $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DBP)_3CuX]$ complexes: (a) X = Cl; (b) X = Br; (c) X = $I\cdot 1.4C_6H_6$.

Table XI. Scalar Coupling Constants a/h and Nuclear Quadrupole Coupling Constants e^2qQ/h Obtained from ^{31}P CP MAS NMR Spectra for $[L_3CuX]$

L	X	solvate	a/h, Hz	$\Delta\nu_3/\Delta\nu_1$	K	e^2qQ/h, MHz
DBP	I	1.4 C_6H_6	886	1.063	0	0
DMPP[a]	Cl	0.2 CH_2Cl_2	879	0.902	0	0
	Br	0.4 CH_2Cl_2	862	0.956	0	0
PPh_3[b]	Cl		933	0.979	0	0
			927	0.957	0	0
	Cl	2 Me_2CO	960	1.043	0	0
	Br		923	1.044	0	0
	Br	2 Me_2CO	937	1.056	0	0
	I		917	1.022	0	0
	I	"C9"[c]	933	1.044	0	0
			900	1.011	0	0

[a] Spectra obtained at a magnetic field strength of 6.342 T (^{31}P resonance frequency = 109.25 MHz). [b] Data from ref 33; spectra obtained at a magnetic field strength of 7.048 T (^{31}P resonance frequency = 121.47 MHz). [c] "C9" = unidentified solvent molecule(s).

by the observation of separate signals due to crystallographically inequivalent sites in the spectra of the DMPP complexes. One slightly unexpected feature of the results for the DBP complexes is that the progressive decrease in the quadrupole coupling constants in the series of cubane $[(PPh_3)CuX]_4$ complexes from X = Cl to I does not occur in the case of $[(DBP)CuX]_4$, where a maximum occurs at X = Br. It would be interesting to know if there is a structural reason for this. The trend of decreasing quadrupole coupling constant from X = Cl to I observed in the CP/MAS results for $[(PPh_3)CuX]_4$ is also observed in the NQR frequencies of $[(Et_3P)CuX]_4$,[69] and this has some theoretical basis.[21] This trend is also observed in the CP/MAS results for $[(DMPP)CuX]_4$.

The CP/MAS spectra for the 2:1 DMPP/CuX complexes are shown in Figure 7, and the results of the analysis of these and of the previously reported spectra of other $[L_2CuX]_n$ complexes[28,29] are given in Table X. The most striking feature of the nuclear quadrupole coupling constants for the phosphole complexes is their smallness in relation to those of $[(PPh_3)_2CuX]$ and $[(T_\alpha Ph_2P)_2CuX]$. This is further evidence for the fact that the phosphine ligands are coordinated to four-coordinate copper atoms in these complexes, in agreement with the structures proposed above on the basis of the far-IR results. Also, the degree of asymmetry in the quartet pattern for the 2:1 DMPP/CuCl complex is significantly smaller than that for the corresponding CuBr and CuI complexes. This is also in agreement with the far-IR results, which indicate an ionic structure $[(DMPP)_4Cu]^+[CuCl_2]^-$ for the CuCl complex and neutral, dimeric structures $[(DMPP)_2CuX]_2$ for the CuBr and CuI complexes; the local symmetry of the copper atom coordinated to DMPP would be

---

(69) Valigura, D.; Verndonck, L.; van der Kelen, G. P. *Bull. Soc. Chim. Belg.* **1980**, *89*, 831.

Table XII. Scalar Coupling Constants and Copper–Phosphorus Bond Distances for a Variety of Complexes

compound					
no.	formula	*d*(CuP)(av), Å	$100/r^2$	*a*(av), Hz[a]	ref
1	$[(DMPP)CuI]_4$	2.2535	8.738	1409	this work
2	$[(Ph_3P)CuCl]_4$	2.192	9.495	2010	32
3	$[(Ph_3P)CuBr]_4$	2.207	9.302	1910	32
4	$[(Ph_3P)CuI]_4$	2.254	8.732	1570	32
5	$[(Ph_3P)_2CuCl]\cdot 0.5C_6H_6$	2.266	8.594	1270	28
6	$[(Ph_3P)_2CuBr]\cdot 0.5C_6H_6$	2.2725	8.521	1280	28
7	$[(Ph_3P)_2CuI]$	2.273	8.515	1200	28
8	$[(T_\alpha Ph_2P)_2CuCl]$	2.249	8.791	1275	31
9	$[(T_\alpha Ph_2P)_2CuBr]$	2.240	8.897	1225	31
10	$[(T_\alpha Ph_2P)_2CuI]$	2.255	8.721	1400	31
11	$[(Ph_3P)_2CuBH_4]$	2.276	8.482	1160	28
12	$[(Ph_3P)_2CuNO_3]$	2.256	8.709	1440	28
13	$[(Ph_3P)_2Cu(CH_3CN)_2]ClO_4$	2.2675	8.577	1255	34
14	$[(Ph_3P)_3CuCl]$	2.351	7.696	940	33
15	$[(Ph_3P)_3CuBr]$	2.353	7.676	935	33
16	$[(Ph_3P)_3CuI]$	2.355	7.656	930	33
17	$[(Ph_3P)_3CuCl]\cdot 2Me_2CO$	2.326	7.946	980	33
18	$[(Ph_3P)_2CuBr]\cdot 2Me_2CO$	2.342	7.785	960	33
19	$[(Ph_3P)_3CuI]\cdot$"C_9"	2.342	7.785	925	33
20	$[(Ph_3P)_4Cu]^+ClO_4^-$	2.5645	5.929	1030	34
21	$[(Ph_3P)_3CuCH_3CN]^+ClO_4^-$	2.330	7.906	993	34
22	$[P(2,4,6)_3CuCl]$	2.177	9.692	2040	7
23	$[P(2,4,6)_3CuBr]$	2.197	9.430	2030	7
24	$[PPh_3Me][Ph_3PCuBr_2]$	2.210	9.265	1690	35

[a] Approximated by $\Delta\nu_2$ (see ref 30). When there is more than one set of resonances, this value is taken as the average of $\Delta\nu_2$.

closer to ideal tetrahedral in the Cl case, and thus would give rise to the smallest copper quadrupole coupling constant of the series.

The CP/MAS spectra for the 3:1 complexes are shown in Figures 8 and 9, and the results of the analysis of some of these and of the previously reported spectra of other $[L_3CuX]$ complexes ($L = PPh_3$)[33] are given in Table XI. Due to the complexity of the spectra for the L = DBP, X = Cl, Br and the L = DMPP, X = I complexes, no analysis of these spectra has been attempted as no unique line assignments can be made in these cases. The $\Delta\nu_3/\Delta\nu_1$ ratios for all of the species in Table XI are equal to 1.0 within experimental error, consistent with a very small copper nuclear quadrupole coupling constant. This is as expected for the nearly ideal tetrahedral coordination environment in the four-coordinate, mononuclear structure which has been observed for the PPh_3 complexes and which is proposed here for the DBP and DMPP complexes. This conclusion is fully supported by the far-IR results (see above).

The scalar coupling constant *a* determined from the CP/MAS spectra also yields information about the structure of the complexes. It has previously been noted that the magnitude of this coupling constant is dependent primarily upon the number of phosphorus atoms bound to the copper atom.[7] In agreement with this, there is a progressive decrease in the value of this coupling constant from the 1:1 to the 3:1 complexes (Tables IX–XI), and this agrees with the proposed structures, which involve from one to three phosphole ligands coordinated to the copper atom. The only exception to this is the 2:1 complex of DMPP with CuCl, for which the ionic structure $[(DMPP)_4Cu]^+[CuCl_2]^-$ is proposed. In this structure, the copper atom which gives rise to the coupling is coordinated to four phosphole ligands, and this is consistent with the fact that the scalar coupling constant *a* for this complex is smaller than those for any of the other complexes studied. It might have been expected that this coupling constant would be comparable to that already measured for $[(PPh_3)_4Cu]^+$ (1030 Hz[34]), but it is considerably lower than this. However, the value for $[(PPh_3)_4Cu]^+$ is anomalously high, as it does not represent a continuation in the trend of decreasing coupling constant with increasing number of bound PPh_3 molecules which is observed in the series $[(PPh_3)CuX]_4$ (1530–1960 Hz), $[(PPh_3)_2CuX]$ (1170–1210 Hz), $[(PPh_3)_3CuX]$ (900–960 Hz) (Tables IX–XI). However, it has been shown that the structure of $[(PPh_3)_4Cu]^+$ is also anomalous in that it displays an unusual distortion in which one of the Cu–P bonds is significantly shorter than the other three.[45] Such a distortion is not shown by complexes such as $[(PMe_3)_4Cu]^+$, which contain less bulky ligands.[45] Thus, the result for $[(DMPP)_4Cu]^+[CuCl_2]^-$ is apparently the first indication that the trend mentioned above extends to undistorted complexes in which the copper atom is coordinated to four phosphorus ligands.

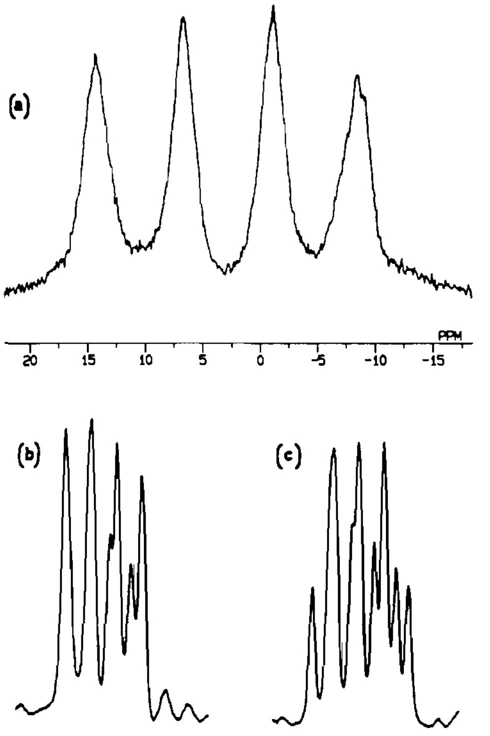


Figure 9. 109.25-MHz $^{31}P\{^1H\}$ CP/MAS NMR spectra of $[(DMPP)_3CuX]$ complexes: (a) X = $Cl\cdot 0.2CH_2Cl_2$; (b) X = $Br\cdot 0.4CH_2Cl_2$; (c) X = I.

As the number of phosphine ligands coordinated to the copper atom increases, the mean Cu–P bond length *r* also increases.[7,28,31-34] Since the coupling constant *a* decreases with an increase in the number of coordinated phosphine ligands, a relationship should exist between *r* and *a*. We have investigated this possibility by examining the data for all complexes for which these two parameters have been measured. The data are listed in Table XII.

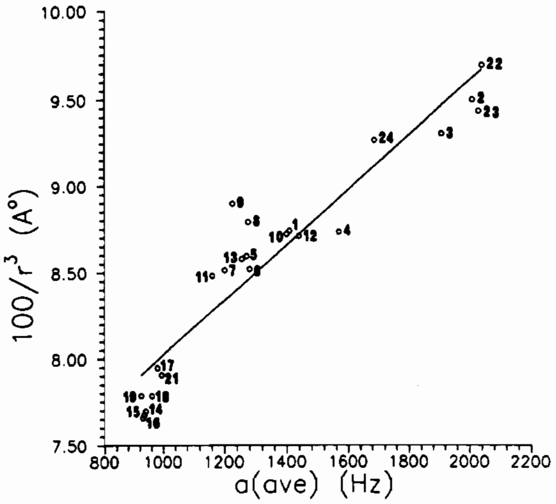


Figure 10. Correlation of $1/r^3$ (r = Cu–P bond length) and the scalar $a(^{63,65}\text{Cu–P})$ coupling constant (as approximated by $\Delta\nu_2$; see ref 30). $1/(r/\text{Å})^3 = (1.582 \times 10^{-5})a/(h/\text{Hz}) + 6.441 \times 10^{-2}$ ($r^2 = 0.90$). The numbers on the points correspond to the compound numbers in Table XII.

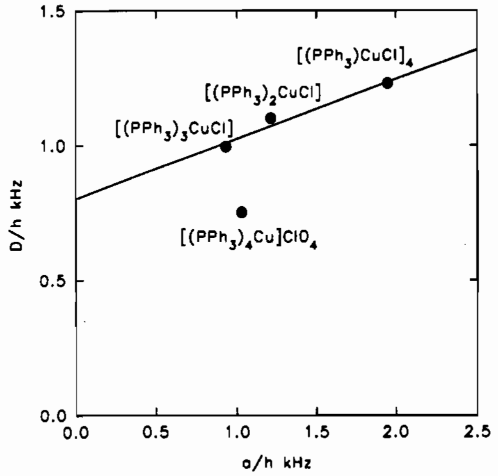


Figure 11. Correlation between the dipolar coupling constant, $D = \mu_0\gamma_P\gamma_{Cu}\hbar^2/4\pi r^3$, and the scalar coupling constant, a, for some selected copper(I) complexes of PPh_3. The best fit line through the points for the CuCl complexes is $D/(h\ \text{kHz}) = 0.219(a/(h/\text{kHz}) + 0.809$ ($r^2 = 0.96$).

We have found that a good linear relationship ($r^2 = 0.90$) between these parameters is obtained if $1/r^3$ is plotted against a. This plot is shown in Figure 10. The form of this relationship was suggested by the assumption which Menger and Veeman made in their analysis[30] that the ratio R of the dipolar coupling constant D (eq 4) to the scalar coupling constant a is equal to 0.5. If this were

$$D = \mu_0\gamma_P\gamma_{Cu}\hbar^2/4\pi r^3 \tag{4}$$

the case for all complexes, then a plot of $1/r^3$ vs a would be linear and pass through the origin. The line of best fit to the data in Figure 10 is

$$1/(r/\text{Å})^3 = (1.582 \times 10^{-5})a/(h/\text{Hz}) + 6.441 \times 10^{-2} \tag{5}$$

Thus, while a reasonably good linear relationship is observed, it does not pass through the origin. The reason for this is that the dipolar coupling constant decreases at a slower rate than the scalar coupling constant a with increasing r. From eq 5 it can be shown that the ratio R of these two coupling constants (eq 2) is approximately equal to 0.5 for the complexes in which one phosphine ligand is coordinated to the copper atom, but that it increases to about 1.0 for complexes with three coordinated phosphine ligands (Figure 11). The relationship expressed in eq 5 is obviously an empirical one, but it can be used to calculate the scalar coupling constant a from the Cu–P bond length r (or vice versa) with an accuracy of better than 1% in most cases. An exception to this occurs for $[(PPh_3)_4Cu]^+$, which lies well below the correlation line (point shown in Figure 11; D calculated using the average Cu–P bond length of 2.58 Å) due to its anomalously large a value, as discussed above. This complex was therefore not included in the correlation shown in Figure 10.

Acknowledgment. The financial support of the UNR Research Advisory Board, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the New Zealand University Grants Committee, and the National Science Foundation (Grant No. CHE-8616437) and financial support to the Colorado State University NMR Center are gratefully acknowledged.

Registry No. $[(DBP)CuCl]_4$, 137056-97-4; $[(DBP)CuBr]_4$, 137056-98-5; $[(DBP)CuI]_4$, 137056-99-6; $[(DMPP)CuCl]_4$, 137039-08-8; $[(DMPP)CuBr]_4$, 137039-09-9; $[(DMPP)CuI]_4$, 137039-10-2; $[(DMPP)_2CuCl]_2$, 137039-11-3; $[(DMPP)_2CuBr]_2$, 137039-12-4; $[(DMPP)_2CuI]_2$, 137039-13-5; $[(DBP)_3CuCl]$, 137057-00-2; $[(DBP)_3CuBr]$, 137057-01-3; $[(DBP)_3CuI]$, 137057-02-4; $[(DMPP)_3CuCl]$, 137039-14-6; $[(DMPP)_3CuBr]$, 137039-15-7; $[(DMPP)_3CuI]$, 137039-16-8.

Supplementary Material Available: For the crystal structure study, listings of crystal and refinement data, H atom coordinates, thermal parameters, and bond distances and angles (5 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.