Structural and Spectroscopic Studies of Halogenocuprate(I) Complexes†

Graham A. Bowmaker,[*,a] **Wang Jirong**[a] **Robert D. Hart,**[b] **Allan H. White**[b] **and Peter C. Healy**[c]
[a] *Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*
[b] *Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia*
[c] *Division of Science and Technology, Griffith University, Nathan, Queensland 4111, Australia*

Reaction of tetraalkylammonium halides, PPh_3 and copper(I) halides in a 1:1:1 mole ratio in dichloromethane yields complexes $[NR_4][Cu(PPh_3)X_2]$ (R = Et, X = Cl or Br; R = Pr, X = Br, I; R = Bu, X = Br) and $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$. These have been characterized by infrared and cross polarization magic angle spinning (CP MAS) ^{31}P NMR spectroscopy, and the structures of most have been determined by single-crystal X-ray diffraction. The compounds $[NR_4][Cu(PPh_3)X_2]$ in the first group above contain mononuclear anions $[Cu(PPh_3)X_2]^-$ with essentially trigonal planar $PCuX_2$ co-ordination. The P–Cu–X and X–Cu–X angles are all within 5° of the ideal trigonal angle of 120°. The compound $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$ contains the centrosymmetric binuclear anion $[Cu_2(PPh_3)_2I_4]^{2-}$ {a dimer of $[Cu(PPh_3)I_2]^-$} in which the two copper atoms are bridged by two iodine atoms, and each copper atom is also bound to a terminal iodine atom and PPh_3 molecule. The FIR spectra of the mononuclear complexes $[Cu(PPh_3)X_2]^-$ show strong bands at 264, 195 and 175 cm^{-1} for X = Cl, Br and I respectively, which are assigned to the asymmetric ν(CuX) stretching mode of the bent X–Cu–X units, and weak bands at 194, 150 and 128 cm^{-1} due to the symmetric ν(CuX) mode. In addition, the X = Cl complex shows a strong band at 126 cm^{-1} which is assigned as the $\delta(CuCl_2)$ bending mode. The dimer $[Cu_2(PPh_3)_2I_4]^{2-}$ shows a remarkably simple spectrum in the ν(CuI) region: a partially resolved doublet at 113 and 126 cm^{-1}. The above vibrational frequencies are compared with those of the species $[CuX_2]^-$ and $[Cu_2I_4]^{2-}$, from which the present species can be considered to be derived by addition of one PPh_3 molecule per copper atom. The solid state CP MAS ^{31}P NMR spectra generally consist of asymmetric quartets due to coupling of the ^{31}P nucleus to the quadrupolar copper nucleus, and the splitting patterns are interpreted in terms of the copper co-ordination environment.

Copper(I) displays a wide diversity in its structural chemistry, and this is well illustrated by the complexes of copper(I) halides. Neutral phosphine and amine ligands form mono- or multinuclear complexes with copper(I) halides in which the copper co-ordination number ranges from two to four.[1–6] The greatest range of structural types has been found for the case of tertiary phosphine ligands, of which the most extensively studied is triphenylphosphine.[1–5] Halogenocuprate(I) complexes formed by the reaction of copper(I) halides with halide ion likewise show a wide diversity of mono- and multi-nuclear structures, although there is a noticeable preference for lower co-ordination numbers; four co-ordination is only found in oligomeric or infinite polymeric structures.[1,2,7]

Less work has been done to investigate the structures and properties of complexes which result from the reaction of the potentially co-ordinatively unsaturated halogenocuprates(I), *e.g.* $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_2X_4]^{2-}$ and $[Cu_4X_6]^{2-}$ with neutral ligands such as phosphines and amines. We have recently shown that the anionic bromocuprate(I) complex $[CuBr_2]^-$ reacts with 1 mol of PPh_3 to yield the species $[Cu(PPh_3)Br_2]^-$, in which the copper(I) ion has the unusual co-ordination number of three.[8] We have also shown that reaction of PPh_3 with the iodocuprate(I) complexes $[CuI_2]^-$ and $[Cu_4I_6]^{2-}$ yields the mononuclear anion $[Cu(PPh_3)_2I_2]^-$ and the binuclear anion $[Cu_2(PPh_3)_2I_3]^-$ respectively. In both of the latter cases the copper atoms exhibit four-co-ordination.[9] Four-co-ordinate copper is also observed in $[Cu_3(AsPh_3)_3I_4]^-$, which can be considered as a $AsPh_3$ adduct of $[Cu_3I_4]^-$.[10] Thus, from the structures of the compounds prepared to date, there appears to be a tendency for iodocuprates to form adducts containing four-co-ordinate copper, while bromocuprates form adducts in which the copper is three-co-ordinate. Attempts to prepare adducts of triphenylphosphine with $[CuCl_2]^-$ were unsuccessful, but it is not clear whether this indicates an increasing preference for lower co-ordination number in the series $[CuL_nX_2]^-$ from X = I to X = Cl or whether this trend has some other cause (*e.g.* a difference in the crystal lattice energies).[9] In this connection it can be noted that, with the bidentate ligand di(2-pyridyl)amine (dpa), complex salts $[Cu(dpa)_2][Cu(dpa)X_2]$ (X = Cl or Br) which contain the halogenocuprate adducts $[Cu(dpa)X_2]^-$ in which the copper atom is four-co-ordinate have been isolated.[11] Thus, the type of complex formed in reactions of halogenocuprates with neutral ligands appears to be strongly dependent upon the nature of the ligand as well as on the particular halide (chloride, bromide, or iodide) involved. The nature of the counter ion may also be important, as in the case of the halogenocuprates themselves.[7] The cations which have been used to date to isolate PPh_3 or $AsPh_3$ adducts of halogenocuprate(I) complexes are the unsymmetrically substituted phosphonium or arsonium ions $[PPh_3Me]^+$ or $[AsPh_3Me]^+$, which have previously been shown to stabilze mononuclear or small oligonuclear halogenocuprates(I).[12–15] It has been shown that systematic changes in the nuclearity and copper co-ordination number

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: G = 10^{-4} T.

in crystalline halogenocuprate(I) complexes can be achieved by using symmetrically substituted tetraalkylammonium cations of various size.[7]

The aim of the present study was to determine whether similar principles apply in the case of PPh_3 adducts of halogenocuprates(I). It was found that, with a range of tetraalkylammonium cations, the complete series of three-co-ordinate complexes $[Cu(PPh_3)X_2]^-$ (X = Cl, Br or I) could be prepared and, in one case, a new binuclear species $[Cu_2(PPh_3)_2I_4]^{2-}$ {a dimer of $[Cu(PPh_3)I_2]^-$} was formed. We report here the preparation of these compounds, and their characterization by X-ray diffraction, far-infrared, and solid-state cross polarization magic angle spinning (CP MAS) ^{31}P NMR spectroscopy.

Experimental

Preparation of Compounds.—Tetraethylammonium dichloro(triphenylphosphine)cuprate(I), $[NEt_4][Cu(PPh_3)Cl_2]$. Tetraethylammonium chloride (0.21 g, 1.25 mmol) and triphenylphosphine (0.33 g, 1.25 mmol) were added to deoxygenated dichloromethane (20 cm^3) under nitrogen. When all of the solid material had dissolved, copper(I) chloride (0.13 g, 1.25 mmol) was added. The solution was then stirred under nitrogen for 20 min, whereupon all of the copper(I) chloride dissolved. The colourless product was precipitated from the resulting pale yellow solution by slow addition of diethyl ether (*ca.* 25 cm^3) with stirring under nitrogen. The product was collected by filtration and dried under vacuum. Samples were sealed in glass tubes under vacuum. M.p. 145–147 °C (Found: C, 59.3; H, 6.75; N, 2.65. Calc. for $C_{26}H_{35}Cl_2CuNP$: C, 59.3; H, 6.65; N, 2.65%).

Tetrapropylammonium dibromo(triphenylphosphine)cuprate(I), $[NPr_4][Cu(PPh_3)Br_2]$. Copper(I) bromide (0.36 g, 2.5 mmol), tetrapropylammonium bromide (0.67 g, 2.5 mmol), and triphenylphosphine (0.66 g, 2.5 mmol) were added to dichloromethane (20 cm^3), and the mixture was stirred until all the solid material had dissolved. The colourless product crystallized from the resulting pale pink solution by slow addition of diethyl ether with stirring. This was collected and washed twice with 20 cm^3 portions of diethyl ether, and sealed in glass tubes under vacuum. The product is air-sensitive, although it is stable for a few days in the air. M.p. 156–157 °C (Found: C, 53.3; H, 6.40; N, 1.95. Calc. for $C_{30}H_{43}Br_2CuNP$: C, 53.6; H, 6.45; N, 2.10%).

Tetraethylammonium dibromo(triphenylphosphine)cuprate(I), $[NEt_4][Cu(PPh_3)Br_2]$. This was prepared by a method similar to that described above for $[NPr_4][Cu(PPh_3)Br_2]$. The product is a colourless crystalline solid and is air-sensitive, although it is stable for a few days in the air. Samples were sealed in glass tubes under vacuum. M.p. 133–134 °C (Found: C, 50.9; H, 5.65; N, 2.10. Calc. for $C_{26}H_{35}Br_2CuNP$: C, 50.7; H, 5.70; N, 2.30%).

Tetrabutylammonium dibromo(triphenylphosphine)cuprate(I), $[NBu_4][Cu(PPh_3)Br_2]$. Copper(I) bromide (0.36 g, 2.5 mmol), tetrabutylammonium bromide (0.81 g, 2.5 mmol), and triphenylphosphine (0.66 g, 2.5 mmol) were added to dichloromethane (20 cm^3), and the mixture was stirred until all the solid material had dissolved. A turbid solution formed upon slow addition of diethyl ether (*ca.* 100 cm^3). The resulting solution was allowed to stand for 0.5 h, whereupon some solid material deposited. After filtration to remove this solid, the clear filtrate was allowed to stand for 2 h, and colourless crystals deposited. The crystals were collected by filtration, and washed twice with 20 cm^3 portions of diethyl ether. M.p. 102–103.5 °C (Found: C, 56.4; H, 6.95; N, 1.80. Calc. for $C_{34}H_{51}Br_2CuNP$: C, 56.1; H, 7.00; N, 1.90%).

Tetrapropylammonium diiodo(triphenylphosphine)cuprate(I), $[NPr_4][Cu(PPh_3)I_2]$. Copper(I) iodide (0.48 g, 2.5 mmol), tetrapropylammonium iodide (0.78 g, 2.5 mmol), and triphenylphosphine (0.66 g, 2.5 mmol) were added to dichloromethane (20 cm^3), and the mixture was stirred under reflux for 0.5 h. A small amount of solid remained undissolved even after addition of a further portion of dichloromethane (10 cm^3). After filtration to remove the insoluble material, the filtrate was allowed to stand for 0.5 h, whereupon a turbid solution formed. The resulting solution was filtered again yielding a clear, colourless solution. Diethyl ether (*ca.* 30 cm^3) was added, and the resulting solution was placed in a desiccator with a container of diethyl ether. Crystallization commenced after 10 min, and was complete after 2 h. The colourless crystals were collected by filtration. The product was washed twice with 20 cm^3 portions of diethyl ether. M.p. 176–179 °C (Found: C, 47.3; H, 5.50. Calc. for $C_{30}H_{43}CuI_2NP$: C, 47.0; H, 5.60%).

Bis(tetraethylammonium) tetraiodobis(triphenylphosphine)dicuprate(I), $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$. Copper(I) iodide (0.48 g, 2.5 mmol), tetraethylammonium iodide (0.64 g, 2.5 mmol), and triphenylphosphine (0.66 g, 2.5 mmol) were added to dichloromethane (50 cm^3), and the mixture was stirred under reflux for 0.5 h. A small amount of insoluble material was removed by filtration, and the clear filtrate was allowed to stand overnight with a container of diethyl ether in a desiccator. The solution deposited colourless crystals. The product was collected, washed twice with 20 cm^3 portions of diethyl ether, and dried under vacuum. M.p. 190–194 °C (Found: C, 43.8; H, 4.65; N, 2.05. Calc. for $C_{52}H_{70}Cu_2I_4N_2P_2$: C, 44.0; H, 4.95; N, 1.95%).

Attempted preparations. (*a*) Attempts to prepare the tetrabutylammonium analogues of $\{[NR_4][Cu(PPh_3)I_2]\}_n$ (R = Pr, n = 1; R = Et, n = 2) from NBu_4I, CuI and PPh_3 in a 1:1:1 ratio in dichloromethane and precipitating the product with diethyl ether did not result in a well defined product.

(*b*) Attempts to prepare the tetrapropylammonium chloride analogue of $[NEt_4][Cu(PPh_3)Cl_2]$ from NPr_4Cl, CuCl and PPh_3 in a 1:1:1 ratio in deoxygenated dichloromethane and precipitating the product with diethyl ether under nitrogen did not result in a well defined product.

(*c*) Attempts to prepare the tetramethylammonium salts of $[Cu(PPh_3)X_2]^-$ (X = Cl, Br or I) from NMe_4X, CuX (X = Cl, Br or I), and PPh_3 in a 1:1:1 ratio in dichloromethane (chloroform, nitromethane, acetonitrile, *etc.*) did not result in well defined products.

(*d*) Attempts to prepare compounds of the type $[NR_4][Cu(PPh_3)_2I_2]$ and $[NR_4][Cu(PPh_3)_2I_3]$ from NR_4I (R = Me, Et, Pr or Bu), CuI and PPh_3 in a 1:1:2 ratio and NR_4I (R = Pr or Bu), CuI and PPh_3 in a 1:2:2 ratio did not result in well defined compounds.

Structure Determinations.—Unique diffractometer data sets were measured at ≈295 K within the limit $2\theta_{max} = 50°$ ($2\theta-\theta$ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ at convergence are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Neutral-atom complex scattering factors were employed,[16] and computation used the XTAL 3.0 program system.[17] Pertinent results are given in Figs. 1 and 2, and in Tables 1–6.

Crystal/refinement data. $[NEt_4][Cu(PPh_3)Cl_2]$, $C_{26}H_{35}Cl_2CuNP$, M = 526.4, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 17.891(8), b = 9.365(4), c = 15.881(7) Å, β = 96.07(3)°, U = 2635 Å^3, D_c = 1.32 g cm^{-3} (Z = 4), $F(000)$ = 1104. μ_{Mo} = 10.4 cm^{-1}. Specimen 0.45 × 0.35 × 0.35 mm; $A^*_{min,max}$ = 1.25, 1.48. N = 4627, N_o = 2611; R = 0.052, R' = 0.048. Syntex $P2_1$ diffractometer.

$[NPr_4][Cu(PPh_3)Br_2]$, $C_{30}H_{43}Br_2CuNP$, M = 671.3, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), a = 38.94(2), b = 9.188(4), c = 19.203(11) Å, β = 110.62(4)°, U = 6430 Å^3,

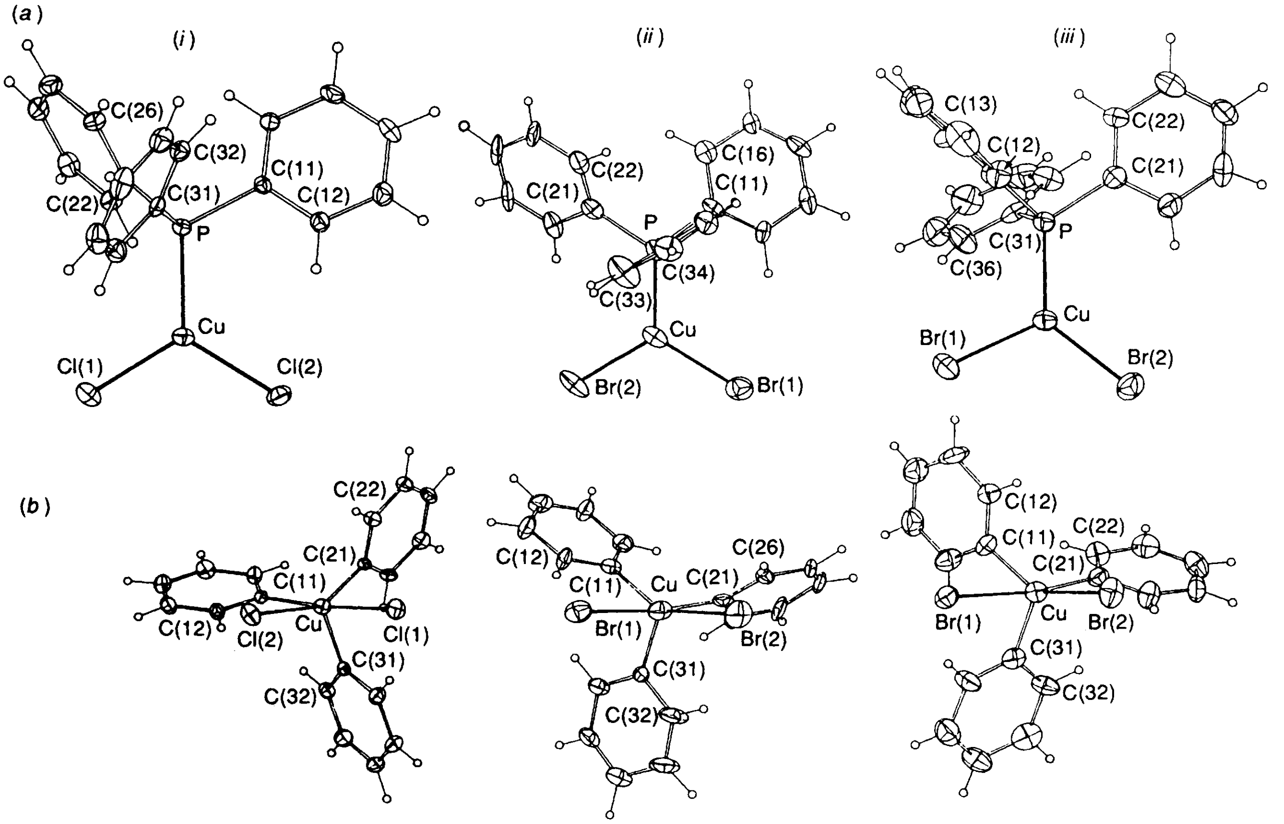


Fig. 1 The $[Cu(PPh_3)X_2]^-$ anions projected (*a*) normal to the $PCuX_2$ plane, and (*b*) down Cu–P; (*i*)–(*iii*) X = Cl or Br (NPr_4 or NBu_4). 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

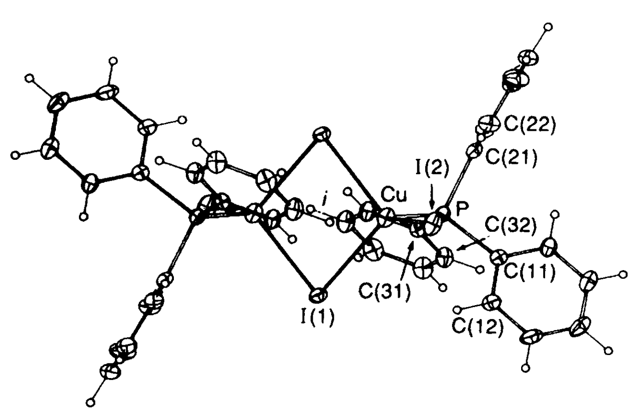


Fig. 2 The $[Cu_2(PPh_3)_2I_4]^{2-}$ anion, projected normal to the CuI_2Cu plane

D_c = 1.39 g cm^{-3} (Z = 8), $F(000)$ = 2752, μ_{Mo} = 31.5 cm^{-1}. Specimen 0.15 × 0.20 × 0.325 mm; $A^*_{min,max}$ = 1.49, 1.93. N = 4033, N_o = 2065; R = 0.057, R' = 0.049. Syntex diffractometer.

$[NBu_4][Cu(PPh_3)Br_2]$, $C_{34}H_{51}Br_2CuNP$, M = 726.3, orthorhombic, space group $P2_1ab$ (variant of $Pca2_1$, C^5_{2v}, no. 29), a = 19.483(11), b = 17.231(12), c = 10.744(8) Å, U = 3612 Å^3, D_c = 1.34 g cm^{-3} (Z = 4), $F(000)$ = 1504, μ_{Mo} = 28.1 cm^{-1}. Specimen 0.40 × 0.54 × 0.10 mm; $A^*_{min,max}$ = 1.32, 2.76. N = 3267, N_o = 1987; R = 0.053, R' = 0.049 (preferred chirality). Enraf-Nonius CAD-4 diffractometer.

$[NPr_4][Cu(PPh_3)I_2]$, $C_{30}H_{43}CuI_2NP$, M = 765.3, monoclinic, space group $C2/c$ (isomorphous with the bromide above), a = 40.29(3), b = 9.426(10), c = 18.93(2) Å, β = 111.76(6)°, U = 6678 Å^3, D_c = 1.52 g cm^{-3} (Z = 8), $F(000)$ = 3040, μ_{Mo} = 24.1 cm^{-1}. Specimen 0.30 × 0.40 × 0.65 mm; $A^*_{min,max}$ = 1.83, 2.76. N = 5446, N_o = 3002; R = 0.048, R' = 0.044. Syntex diffractometer.

$[NEt_4]_2[Cu_2(PPh_3)_2I_4]$, $C_{52}H_{70}Cu_2I_4N_2P_2$, M = 1418.6, monoclinic, space group $P2_1/c$, a = 10.499(4), b = 13.609(5), c = 21.48(2) Å, β = 115.09(6)°, U = 2780 Å^3, D_c = 1.65 g cm^{-3} (Z = 2), $F(000)$ = 1392, μ_{Mo} = 28.2 cm^{-1}. Specimen 0.25 × 0.30 × 0.55 mm; $A^*_{min,max}$ = 1.84, 3.67. N = 4895, N_o = 3870; R = 0.051, R' = 0.049. CAD-4 diffractometer.

Abnormal features/variations in procedure. The ethyl groups of the cation in the last compound are disordered, each of the methylene groups being modelled as a pair of equal components.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

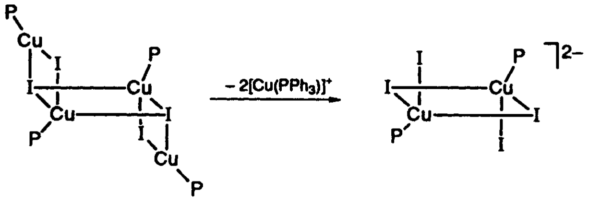
Spectroscopy.—Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed polythene discs on a Digilab FTS-60 Fourier transform IR spectrometer employing an FTS-60V vacuum optical bench with a 6.25 μm mylar-film beam splitter, a mercury-lamp source and a TGS detector. The CP MAS ^{31}P NMR spectra were obtained at room temperature on a Bruker CXP-300 spectromter at a frequency of 121.47 MHz by using ^1H–^{31}P cross-polarization with radiofrequency fields of 8 and 20 G for ^1H and ^{31}P respectively. Chemical shifts were referenced to solid triphenylphosphine.

Results and Discussion

Syntheses.—Reaction of tetraalkylammonium halides, triphenylphosphine, and copper(I) halides in a 1 : 1 : 1 mole ratio in dichloromethane yields complexes of empirical formula $[NR_4][Cu(PPh_3)X_2]$ (R = Et, X = Cl, Br or I; R = Pr, X = Br, I; R = Bu, X = Br) which were precipitated from solution by

Table 1 Non-hydrogen atom coordinates for $[NEt_4][Cu(PPh_3)Cl_2]$

Atom	*x*	*y*	*z*
Cl(1)	0.859 8(1)	0.972 0(1)	0.377 8(1)
Cl(2)	0.877 7(1)	0.573 8(2)	0.339 5(1)
Cu	0.811 35(5)	0.754 0(1)	0.387 34(5)
P	0.697 3(1)	0.721 8(2)	0.425 6(1)
C(11)	0.669 0(3)	0.536 6(7)	0.443 1(4)
C(12)	0.703 4(4)	0.430 7(8)	0.398 6(4)
C(13)	0.685 5(4)	0.288 7(8)	0.408 8(5)
C(14)	0.634 0(4)	0.249 2(8)	0.464 4(5)
C(15)	0.600 6(4)	0.353 0(9)	0.508 3(5)
C(16)	0.618 1(4)	0.495 6(8)	0.498 9(4)
C(21)	0.670 9(4)	0.814 4(7)	0.519 5(4)
C(22)	0.726 8(4)	0.834 0(8)	0.585 1(4)
C(23)	0.710 7(4)	0.903 7(8)	0.659 0(4)
C(24)	0.640 0(5)	0.955 3(8)	0.666 2(4)
C(25)	0.583 2(4)	0.937 1(8)	0.600 2(5)
C(26)	0.598 7(4)	0.865 0(8)	0.526 5(4)
C(31)	0.627 7(4)	0.785 8(7)	0.340 9(4)
C(32)	0.555 3(4)	0.728 0(8)	0.323 7(4)
C(33)	0.507 0(5)	0.778 0(9)	0.257 2(5)
C(34)	0.530 1(5)	0.882 9(9)	0.206 5(5)
C(35)	0.599 7(5)	0.945 1(8)	0.223 1(5)
C(36)	0.649 6(4)	0.895 1(8)	0.290 3(5)
N	0.889 6(3)	0.279 4(6)	0.613 0(3)
C(111)	0.806 9(4)	0.253 0(8)	0.621 1(4)
C(112)	0.785 5(4)	0.254 3(9)	0.711 7(4)
C(121)	0.896 4(4)	0.283 8(8)	0.517 6(4)
C(122)	0.975 2(4)	0.290 0(9)	0.492 4(5)
C(131)	0.914 4(4)	0.420 5(8)	0.654 7(4)
C(132)	0.869 8(5)	0.550 7(9)	0.623 8(5)
C(141)	0.940 1(4)	0.168 0(8)	0.656 4(4)
C(142)	0.924 7(5)	0.015 6(8)	0.624 6(4)



Scheme 1

addition of diethyl ether. Attempts to prepare tetramethylammonium compounds of this type were unsuccessful. Attempts to prepare compounds of the type $[NR_4][Cu(PPh_3)_2I_2]$ and $[NR_4][Cu_2(PPh_3)_2I_3]$, analogous to the previously reported $[PPh_3Me]^+$ compounds,[9] from $[NR_4]I$, CuI and PPh_3 in 1:1:2 and 1:2:2 ratios respectively did not result in well defined compounds. Thus, only the 1:1:1 complexes can be prepared with tetraalkylammonium halides but, in contrast with the $[PPh_3Me]^+$ case, the complete series of $[Cu(PPh_3)X_2]^-$ (X = Cl, Br or I) can be obtained in this way.

X-Ray Structure Determinations.—The complexes $[NR_4][Cu(PPh_3)X_2]$ (R = Et, X = Cl or Br; R = Pr, X = Br, I; R = Bu, X = Br) contain mononuclear anions $[Cu(PPh_3)X_2]^-$ with essentially trigonal-planar $PCuX_2$ co-ordination. The structures of the anions in some of these complexes are shown in Fig. 1, and the copper atom environments in all of the $[Cu(PPh_3)X_2]^-$ species for which structures were determined are given in Table 5. In all cases the $PCuX_2$ units are nearly planar, the Cu atom lying less than 0.1 Å from the PX_2 plane. This corresponds to values for the angles between PCu and the CuX_2 plane which lie in the range 173–177°, compared with 180° expected for a planar structure. The deviation from planarity shows no systematic variation with X, being greatest for X = Cl and least for X = Br. The anions have no crystallographically imposed symmetry, but deviations from idealized C_{2v} symmetry (in which the two Cu–X bond lengths and the two P–Cu–X angles would be equal) are small in all cases except that of the $[Cu(PPh_3)Br_2]^-$ ion in $[NBu_4][Cu(PPh_3)Br_2]$. The P–Cu–X and X–Cu–X angles are all within 5° of the ideal trigonal angle of 120°, but some systematic trends in the deviations from this value are evident. Thus the X–Cu–X angles are all significantly less than 120° and, with the exception of the strongly distorted anion in $[NBu_4][Cu(PPh_3)Br_2]$, the deviation from 120° decreases from X = Cl to X = I.

As has been pointed out previously for the X = Br case,[8] the present compounds are the $n = 1$ members of the series $[Cu(PPh_3)_nX_{3-n}]^{(2-n)-}$ and, with the present results, the structures of all members of these series are now available. Structures of a range of compounds containing the $n = 3$ member, $[Cu(PPh_3)_3]^+$, show that the counter anion is co-ordinated to the copper atom and the P_3Cu core deviates significantly from planarity. For complexes with weakly co-ordinating anions such as ClO_4^- or BF_4^- the mean P–Cu–P angle is 116° and Cu–P is 2.31 Å.[18] The structural parameters for the n = 0–2 complexes are listed in Table 7. There are some systematic changes in these with changes in n. Thus, there is a progressive decrease in the Cu–P bond length and an increase in the P–Cu–X bond angle with decreasing n, *i.e.* with decreasing number of PPh_3 molecules in the copper co-ordination sphere. Both of these trends can be explained in terms of the greater σ-donor capacity of PPh_3 relative to X^-, but the magnitudes of these changes are surprisingly small. The dependence of the Cu–X bond length on n is even smaller, although this parameter does appear to increase slightly with decreasing n. The average X–Cu–X angles in $[CuX_3]^{2-}$ are close to 120°, but the values for $[Cu(PPh_3)X_2]^-$ are all slightly less than this and increase from X = Cl to X = I as noted above. This can be attributed to the increase in the σ-donor capacity of X^- from Cl to I.

There is a remarkably close similarity between the structural parameters for $[Cu(PPh_3)X_2]^-$ and those determined previously for the $Cu(PPh_3)X_2$ fragments in $[(Ph_3P)CuX_2Cu(PPh_3)_2]$,[23] as has been pointed out previously for the X = Br case.[8] The main difference is the significantly more acute X–Cu–X angle at the trigonally co-ordinated copper atom in the latter complexes; the observed values are 107.1(2), 111.5(1) and 116.4(6)° for X = Cl, Br, I respectively, which show the same trend but cover a wider range than the values found here for $[Cu(PPh_3)X_2]^-$.

The X-ray structure determination for the compound of empirical formula $[NEt_4][Cu(PPh_3)I_2]$ shows that this is in fact $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$, containing the centrosymmetric binuclear anion $[Cu_2(PPh_3)_2I_4]^{2-}$ {a dimer of $[Cu(PPh_3)I_2]^-$} in which the two copper atoms are bridged by two iodine atoms, and each copper atom is also bound to a terminal iodine atom and PPh_3 molecule. The structure of the anion is shown in Fig. 2, and the structural parameters which define the copper atom environment are listed in Table 6. This represents a new type of binuclear copper(I) complex involving halide and triphenylphosphine ligands. The three previously reported types are represented by $[(Ph_3P)CuX_2Cu(PPh_3)_2]$ (X = Cl, Br or I),[4,23] $[(MePh_2P)_2CuI_2Cu(PPh_2Me)_2]$,[24] and $[(Ph_3P)CuI_3Cu(PPh_3)]^-$.[9] The last two complexes both involve four-co-ordination for both of the copper atoms in the structure, the first with two doubly bridging iodine atoms and the second with three such atoms. The structure of the present complex, which can be formulated in a similar manner as $[(Ph_3P)ICuI_2CuI(PPh_3)]^{2-}$, can be considered to be derived from that of $[(MePh_2P)_2CuI_2Cu(PPh_2Me)_2]$ by replacement of one phosphine ligand on each of the copper atoms by a terminally bound iodide ligand.

The structure of the present complex can also be considered to be derived from that of the well known 'step' form of the tetrameric 1:1 adduct of PPh_3 with CuI, $[Cu_4(PPh_3)_4I_4]$,[25] by removal of the two $[Cu(PPh_3)]^+$ units in which the copper atom is three-co-ordinate (Scheme 1). This result is similar to that for the complex $[Cu_3(AsPh_3)_3I_4]^-$, whose structure is derived from that of 'cubane' $[Cu_4(AsPh_3)_3I_4]$ by removal of

Table 2 Non-hydrogen atom coordinates for $[NPr_4][Cu(PPh_3)X_2]$ (X = Br or I)

	Bromide			Iodide		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
X(1)	0.378 51(4)	0.335 6(2)	0.315 36(8)	0.376 95(2)	0.334 95(7)	0.318 23(4)
X(2)	0.441 64(3)	0.180 6(2)	0.516 54(9)	0.440 74(2)	0.171 83(9)	0.542 45(4)
Cu	0.382 83(3)	0.241 8(2)	0.433 92(8)	0.380 39(3)	0.233 1(1)	0.444 96(6)
P	0.333 13(7)	0.227 1(3)	0.463 9(2)	0.330 24(5)	0.223 8(2)	0.468 4(1)
C(11)	0.291 7(3)	0.156(1)	0.389 9(7)	0.290 3(2)	0.152 1(8)	0.394 3(4)
C(12)	0.286 7(3)	0.186(1)	0.318 0(7)	0.284 5(2)	0.187 6(9)	0.319 3(5)
C(13)	0.255 3(4)	0.136(2)	0.261 6(7)	0.254 2(3)	0.139(1)	0.261 1(5)
C(14)	0.230 7(3)	0.051(1)	0.281 6(9)	0.231 0(2)	0.054(1)	0.275 7(5)
C(15)	0.234 9(3)	0.020(1)	0.350 2(8)	0.236 2(2)	0.014(1)	0.348 6(6)
C(16)	0.265 7(4)	0.073(1)	0.408 8(7)	0.266 5(2)	0.064 6(9)	0.408 9(5)
C(21)	0.336 2(3)	0.131(1)	0.548 9(6)	0.330 8(2)	0.137 7(8)	0.554 9(4)
C(22)	0.312 4(3)	0.157(1)	0.589 0(8)	0.308 6(2)	0.177 3(9)	0.592 2(5)
C(23)	0.315 1(4)	0.083(2)	0.650 5(8)	0.309 3(2)	0.109(1)	0.656 6(5)
C(24)	0.342 7(6)	−0.022(2)	0.677 9(7)	0.332 1(3)	−0.003(1)	0.684 3(5)
C(25)	0.366 9(4)	−0.042(2)	0.641 7(9)	0.354 6(2)	−0.042 8(9)	0.649 2(5)
C(26)	0.364 2(3)	0.029(1)	0.580 0(8)	0.354 3(2)	0.026 5(9)	0.584 2(5)
C(31)	0.320 0(3)	0.407(1)	0.482 3(6)	0.318 6(2)	0.404 3(8)	0.484 8(5)
C(32)	0.344 9(3)	0.483(1)	0.539 4(9)	0.343 6(2)	0.483(1)	0.539 8(6)
C(33)	0.338 1(4)	0.618(2)	0.559 8(9)	0.336 6(3)	0.615(1)	0.558 3(6)
C(34)	0.305 4(4)	0.690(1)	0.519 1(9)	0.304 0(3)	0.678(1)	0.519 4(6)
C(35)	0.280 8(3)	0.614(2)	0.465 7(8)	0.279 3(2)	0.606(1)	0.464 2(6)
C(36)	0.287 4(3)	0.476(1)	0.445 9(6)	0.286 1(2)	0.469 1(9)	0.445 9(5)
N	0.430 1(2)	0.218(1)	0.861 2(7)	0.429 1(2)	0.216 7(7)	0.858 0(4)
C(111)	0.389 3(4)	0.237(2)	0.845 0(8)	0.390 9(2)	0.246(1)	0.849 9(5)
C(112)	0.371 3(5)	0.164(2)	0.882(1)	0.374 5(3)	0.157(1)	0.890 7(5)
C(113)	0.331 1(3)	0.192(1)	0.863 6(8)	0.336 8(3)	0.200(1)	0.877 1(6)
C(121)	0.442 3(4)	0.333(2)	0.811(1)	0.441 7(3)	0.330(1)	0.818 1(5)
C(122)	0.427 3(5)	0.326(2)	0.739(1)	0.424 4(3)	0.346(1)	0.735 3(6)
C(123)	0.443 4(5)	0.452(2)	0.707(1)	0.440 8(3)	0.466(1)	0.705 9(6)
C(131)	0.451 0(4)	0.249(3)	0.938 7(8)	0.453 4(3)	0.216(1)	0.941 6(6)
C(132)	0.445 5(5)	0.360(2)	0.979(1)	0.452 4(3)	0.343(1)	0.986 6(7)
C(133)	0.469 5(6)	0.382(2)	1.061 5(8)	0.479 7(4)	0.334(2)	1.068 3(7)
C(141)	0.437 1(5)	0.062(2)	0.836(1)	0.430 4(3)	0.071(1)	0.823 8(6)
C(142)	0.469 1(5)	0.017(2)	0.833(1)	0.464 0(3)	0.025(1)	0.819 9(8)
C(143)	0.471 5(5)	−0.128(2)	0.810(1)	0.458 6(3)	−0.113(1)	0.775 1(9)

Table 3 Non-hydrogen atom coordinates for $[NBu_4][Cu(PPh_3)Br_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Br(1)	0.418 2(1)	0.564 24(9)	0.141 7(2)	C(35)	0.648(1)	0.520(1)	−0.102(2)
Br(2)	0.457 2(1)	0.405 9(1)	0.406 6(2)	C(36)	0.617 0(8)	0.537(1)	0.016(2)
Cu	1/2*	0.506 52(9)	0.282 4(2)	N	0.915 5(7)	0.667 0(6)	0.075(1)
P	0.607 6(2)	0.551 7(2)	0.269 6(4)	C(111)	0.974 5(9)	0.709(1)	0.023(2)
C(11)	0.612 3(7)	0.657 1(7)	0.269(2)	C(112)	1.012(1)	0.678(2)	−0.079(3)
C(12)	0.580 5(9)	0.696 1(9)	0.362(2)	C(113)	1.069(2)	0.716(3)	−0.140(3)
C(13)	0.583(1)	0.777(1)	0.369(2)	C(114)	1.070(2)	0.768(2)	−0.202(5)
C(14)	0.618(1)	0.817(1)	0.280(2)	C(121)	0.861 9(9)	0.653(1)	−0.031(2)
C(15)	0.652(1)	0.779(1)	0.185(2)	C(122)	0.841(1)	0.722(2)	−0.098(3)
C(16)	0.649 5(8)	0.698 6(9)	0.179(2)	C(123)	0.783(1)	0.695(2)	−0.196(3)
C(21)	0.671 1(7)	0.526 3(8)	0.386(1)	C(124)	0.757(2)	0.750(3)	−0.279(3)
C(22)	0.724 1(7)	0.573 7(9)	0.418(2)	C(131)	0.860(2)	0.707(1)	0.198(4)
C(23)	0.774 0(8)	0.551(1)	0.501(2)	C(132)	0.906(1)	0.727(1)	0.243(4)
C(24)	0.773 8(9)	0.477(1)	0.550(2)	C(133)	0.843(2)	0.772(1)	0.363(2)
C(25)	0.724(1)	0.430(1)	0.516(2)	C(134)	0.885(2)	0.800(2)	0.468(2)
C(26)	0.670 1(8)	0.452 6(9)	0.437(2)	C(141)	0.934(1)	0.588(1)	0.124(2)
C(31)	0.649 7(8)	0.524 9(8)	0.121(2)	C(142)	0.934(3)	0.552(1)	0.208(3)
C(32)	0.715 1(8)	0.490(1)	0.121(1)	C(143)	0.923(2)	0.447(3)	0.252(4)
C(33)	0.741(1)	0.469(1)	0.005(3)	C(144)	0.980(3)	0.461(2)	0.295(5)
C(34)	0.711(1)	0.486(1)	−0.108(2)				

* Defines origin.

one $[Cu(AsPh_3)]^+$ unit.[10] The structural parameters for $[Cu_2(PPh_3)_2I_4]^{2-}$ are closely similar to the corresponding parameters in the 'step' form of $[Cu_4(PPh_3)_4I_4]$,[25] the main differences being readily attributable to the additional bridging interactions present in the neutral tetramer. Thus, the two bridging Cu–I bond lengths Cu–I(1) and Cu–I(1') in $[Cu_2(PPh_3)_2I_4]^{2-}$ are almost identical, but Cu–I(1) increases by 0.03 Å as I(1) changes from a doubly- to a triply-bridging mode in the 'step' tetramer. The other Cu–I and the Cu–P bond lengths change by less than 0.004 Å. The angles within the CuI(1)-Cu'I(1') core differ by less than 2° between the two structures, whereas the angles involving the P–Cu and Cu–I(2) bonds change by up to 10° as a consequence of the presence of the additional copper atom across I(1), I(2) in the 'step' tetramer.

Table 4 Non-hydrogen atom coordinates for $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$

Atom	*x*	*y*	*z*
Cu	0.937 8(1)	0.584 25(7)	0.434 58(5)
I(1)	0.803 22(5)	0.496 17(4)	0.502 18(3)
I(2)	0.815 63(7)	0.553 14(5)	0.301 70(3)
P	0.962 7(2)	0.744 0(1)	0.462 4(1)
C(11)	0.810 0(8)	0.819 0(6)	0.410 6(4)
C(12)	0.679 6(9)	0.776 6(7)	0.386 7(4)
C(13)	0.559 3(9)	0.828 3(8)	0.348 7(5)
C(14)	0.568(1)	0.925 3(9)	0.333 9(4)
C(15)	0.699(1)	0.969 3(7)	0.356 7(4)
C(16)	0.818 4(9)	0.917 6(6)	0.394 2(4)
C(21)	1.105 0(8)	0.805 7(6)	0.449 8(4)
C(22)	1.125 9(9)	0.781 2(7)	0.392 5(4)
C(23)	1.224(1)	0.828 8(9)	0.378 1(5)
C(24)	1.307(1)	0.902 6(8)	0.420 8(5)
C(25)	1.289 5(9)	0.924 9(7)	0.478 5(5)
C(26)	1.190 5(9)	0.876 9(6)	0.493 7(4)
C(31)	0.995 5(8)	0.777 0(5)	0.550 0(4)
C(32)	0.937 0(9)	0.857 9(6)	0.567 7(4)
C(33)	0.964(1)	0.878 5(6)	0.635 4(4)
C(34)	1.055(1)	0.818 7(7)	0.687 1(4)
C(35)	1.115(1)	0.738 4(7)	0.671 4(4)
C(36)	1.084 8(9)	0.717 5(6)	0.603 3(4)
N	0.629 4(7)	0.861 9(5)	0.145 7(3)
C(111)*	0.794(2)	0.878(2)	0.164 1(9)
C(112)*	0.741(2)	0.855(1)	0.215 7(8)
C(121)	0.881(1)	0.901 8(9)	0.231 1(6)
C(211)*	0.572(2)	0.958(2)	0.162(1)
C(212)*	0.596(2)	0.966(1)	0.118 5(9)
C(221)	0.583(2)	1.047(1)	0.152 6(9)
C(311)*	0.620(2)	0.776(2)	0.186(1)
C(312)*	0.485(2)	0.824(1)	0.149 4(9)
C(321)	0.483(1)	0.730(1)	0.170 6(6)
C(411)*	0.561(2)	0.848(2)	0.068 9(9)
C(412)*	0.658(2)	0.796(2)	0.098(1)
C(421)	0.575(2)	0.772(1)	0.033 7(7)

* Population: 0.5 (–).

Table 5 Copper environments* in $[Cu(PPh_3)X_2]^-$

Cation	$[NEt_4]^+$	$[NPr_4]^+$	$[NBu_4]^+$	$[NPr_4]^+$
Anion X	Cl	Br	Br	I
Distances (Å)				
Cu–P	2.211(2)	2.209(4)	2.241(4)	2.225(3)
Cu–X(1)	2.230(2)	2.384(3)	2.412(3)	2.540(3)
Cu–X(2)	2.241(2)	2.349(2)	2.341(3)	2.515(2)
Angles (°)				
P–Cu–X(1)	121.36(8)	119.83(10)	115.90(13)	117.88(7)
P–Cu–X(2)	121.88(8)	122.99(11)	128.73(12)	123.17(10)
X(1)–Cu–X(2)	116.26(9)	117.10(9)	115.28(3)	118.64(7)
Σ	359.50	359.92	359.91	359.79
Plane descriptors (Å)				
δCu	0.091(1)	0.039(2)	0.041(2)	0.078(1)

* δCu is the distance of the copper from the PX_2 plane; Σ is the sum of the P–Cu–X and X–Cu–X angles.

The complex anion $[Cu_2(PPh_3)_2I_4]^{2-}$ can also be considered as a PPh_3 adduct of the known $[Cu_2I_4]^{2-}$ species. These consist of two trigonally co-ordinated copper atoms connected by two bridging iodines, with one terminal iodine atom on each copper. The ions are generally planar, or nearly planar,[26–28] although structures which are significantly non-planar (folded about the line connecting the two bridging iodine atoms) have also been found.[28] The average terminal and bridging Cu–I bond lengths are about 2.5 and 2.6 Å respectively. These increase to about 2.6 and 2.7 Å respectively upon formation of $[Cu_2(PPh_3)_2I_4]^{2-}$ (Table 6).

Table 6 Copper environments (distances in Å, angles in °) in $[Cu_2(PPh_3)_2I_4]^{2-}$ (primed atoms are centrosymmetrically related)

Cu–P	2.240(2)	P–Cu–I(1)	108.40(9)
Cu–I(1)	2.699(2)	P–Cu–I(1′)	106.27(6)
Cu–I(1′)	2.702(1)	P–Cu–I(2)	113.29(6)
Cu–I(2)	2.620(3)	I(1)–Cu–I(1′)	101.22(5)
Cu ··· Cu′	3.428(2)	I(1)–Cu–I(2)	112.84(6)
I(1) ··· I(1′)	4.174(2)	I(1′)–Cu–I(2)	113.92(6)
		Cu–I(1)–Cu′	78.78(5)

P and I(2) respectively 1.977(3) and 2.045(2) Å out of the $Cu_2I(1)_2$ plane.

It has previously been shown that for crystalline halogenocuprate(I) complexes obtained with symmetrically substituted quaternary ammonium, phosphonium and arsonium cations there is a definite correlation between the cation size and the co-ordination number of the copper(I) atom. The trend is such that there is an increase in the copper co-ordination number with decreasing size of the cation. This is a consequence of the fact that large cations can more effectively separate the anionic species and thus suppress catenation, leading to the formation of small, discrete anions in which the copper exhibits a low co-ordination number. Small cations, on the other hand, are less effective in the suppression of catenation and tend to promote the formation of polynuclear species in which the copper attains a high co-ordination number.[7] This behaviour is evident in the different structures found in the present study for $[NPr_4][Cu(PPh_3)I_2]$ and $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$. No such change in structure occurs for the corresponding bromo-complexes. The FIR results show that these are isostructural (see below), and this also corresponds well with the data for halogenocuprates(I): larger cations are generally required in order to achieve a specific low co-ordination number in iodocuprates(I) than in bromocuprates(I).[7] For the series of complexes of empirical formula $[NR_4][CuX_2]$ the change from a dimer to a monomer anion structure occurs from R = Et to R = Pr for X = Br, and for R larger than Bu for X = I [no mononuclear iodocuprates(I) have previously been reported with tetraalkylammonium cations].[7] For the 1 : 1 PPh_3 adducts, the corresponding change apparently requires that R be smaller than Et for X = Br, and occurs from R = Et to R = Pr for X = I. Thus the dimer to monomer transition occurs at a much lower cation size for the PPh_3 adducts than for the parent halogenocuprates. This is most likely to be due to the considerable steric bulk of the PPh_3 ligand, which contributes to a breakdown of catenation so that monomeric species can be achieved with cations of considerably smaller size than is the case for the corresponding halogenocuprates(I) in the absence of the ligand.

Although $[Cu_2(PPh_3)_2I_4]^{2-}$ is a new type of copper(I) complex, its structure is essentially the same as that found for several 1 : 1 adducts of neutral ligands with mercury(II) halides. Thus, with the triphenylphosphine ligand, these adducts are dimers $[Hg_2(PPh_3)_2X_4]$ with two bridging halogens linking the two mercury atoms, and a terminal halogen atom and PPh_3 molecule on each mercury atom.[29,30] Although these structures are formally analogous, there are significant differences which reflect the different co-ordination properties of copper(I) and mercury(II). Thus, the M–X_t (X_t = terminal halide) bond lengths are about 10% longer than the bridging bond lengths in the mercury complexes, but this difference is only about 3% in the case of the copper complex. Related to this is the fact that the P–M–X_t angles in the mercury complexes are about 15° larger than the value for the copper complex. Both of these observations can be related to the greater tendency for mercury(II) to exhibit linear two-co-ordination, so that the structures of the mercury complexes discussed here are distorted from the situation observed in the copper complex, where all of the bond angles are close to the tetrahedral angle (109.5°), to

Table 7 Comparison of core geometries (distances in Å, angles in °) in $[Cu(PPh_3)_nX_{3-n}]^{(2-n)-}$ (n = 0–2; X = Cl, Br or I); average values are given in the cases where multiple values occur due to crystallographic inequivalence

Complex	Cu–P	Cu–X	P–Cu–P	P–Cu–X	X–Cu–X	Ref.
$[Cu(PPh_3)_2Cl]$	2.27	2.21	125.5	117.3	—	19
$[Cu(PPh_3)Cl_2]^-$	2.21	2.24	—	121.6	116.3	*a*
$[CuCl_3]^{2-}$	—	2.22	—	—	119.9	20
$[Cu(PPh_3)_2Br]$	2.27	2.35	126.0	116.9	—	19
$[Cu(PPh_3)Br_2]^-$	2.21	2.37	—	121.4	117.1	*b*
$[CuBr_3]^{2-}$	—	2.37	—	—	120.0	21
	—	2.36	—	—	120.0	15
$[Cu(PPh_3)_2I]$	2.27	2.52	126.9	116.6	—	19
$[Cu(PPh_3)I_2]^-$	2.23	2.53	—	120.5	118.6	*b*
$[CuI_3]^{2-}$	—	2.55	—	—	120.0	14, 22

[a] This work, $[NEt_4]^+$ salt. [b] This work, $[NPr_4]^+$ salt.

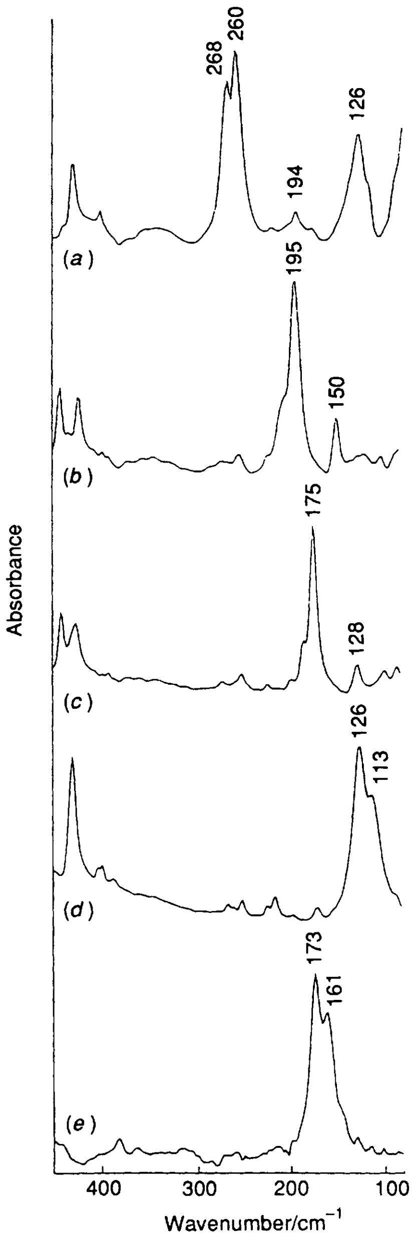


Fig. 3 The FIR spectra of (*a*) $[NEt_4][Cu(PPh_3)Cl_2]$, (*b*) $[NPr_4][Cu(PPh_3)Br_2]$, (*c*) $[NPr_4][Cu(PPh_3)I_2]$, (*d*) $[NEt_4]_2[Cu_2(PPh_3)_2I_4]$ and (*e*) $[NEt_4]_2[Cu_2I_4]$. Bands due to vibrations of the CuX_2 or Cu_2X_4 units are labelled with their wavenumbers

one which can be described as two P–Hg–X units linked by two bridging halides, the linearity of the P–Hg–X units being distorted by the bridging interaction.

Far-infrared Spectra.—The far-infrared spectra of several of the $[Cu(PPh_3)X_2]^-$ complexes are shown in Fig. 3. These show halogen-sensitive bands in the region 100–300 cm^{-1} which can be assigned to vibrations of the CuX_2 units. The complex $[NPr_4][Cu(PPh_3)Br_2]$ shows a strong band at 195 cm^{-1} and a weaker band at 150 cm^{-1} which correspond exactly to the bands which were observed for the corresponding $[PPh_3Me]^+$ compound, and which were assigned to the antisymmetric (ν_{asym}) and symmetric (ν_{sym}) Cu–Br stretching modes of the $CuBr_2$ unit.[8] These assignments are supported by the observation in the present work of analogous bands at 264 and 194 cm^{-1} for the X = Cl complex, and 175 and 128 cm^{-1} for the X = I complex. The ν_{asym}(CuCl) mode in $[NEt_4][Cu(PPh_3)Cl_2]$ shows evidence of splitting (260, 268 cm^{-1}), and there is another strong band at 126 cm^{-1} which probably arises from the $\delta(CuCl_2)$ bending mode of the $CuCl_2$ unit. The expected halogen dependence of such a band would lead to the prediction that a similar band should occur in the range 80–90 cm^{-1} for the corresponding bromo-complex. There is no clear evidence for such a band in the spectrum of the $[NPr_4]^+$ compound, but the $[PPh_3Me]^+$ compound shows a definite band at 85 cm^{-1} which can now be assigned as $\delta(CuBr_2)$.[8] The FIR spectrum of $[NBu_4][Cu(PPh_3)Br_2]$ is unusual in that it contains four bands in the ν(CuBr) region: one of medium intensity at 149 cm^{-1}, and three strong bands at 181, 197 and 218 cm^{-1}. Structurally, this compound differs from its $[NPr_4]^+$ and $[PPh_3Me]^+$ analogues in that it has a strongly distorted $CuBr_2$ group (see above). This would account for the greater range of ν(CuBr) frequencies, but not for the multiplicity of bands, which must arise from correlation effects. The FIR spectrum of $[NEt_4][Cu(PPh_3)Br_2]$ is similar in appearance to that of the $[NPr_4]^+$ analogue [ν_{asym}(CuBr) 203 cm^{-1}, ν_{sym}(CuBr) 152 cm^{-1}]. This therefore contains the mononuclear form of the anion, and not the binuclear dimer as was found in the case of the corresponding iodo-complex.

The wavenumbers of the ν(Cu–X) bands for these and for some related copper(I) halide complexes are given in Table 8. The ν_{asym}(CuX) frequencies lie between the ν(CuX) frequency for $[Cu(PPh_3)_2X]$ and ν_{asym}(CuX) for $[CuX_3]^{2-}$. This decrease in ν(CuX) correlates well with the observed overall increase in Cu–X bond length for this series (see above). It has previously been shown that there is a good correlation between ν(CuX) and the Cu–X bond length in neutral adducts of copper(I) halides which contain a single terminal Cu–X bond.[32] Our results suggests that a similar relationship exists for series such as the present one in which there are several terminal Cu–X bonds, although the situation is complicated by the existence of more than one ν(CuX) mode. The assignments of the ν_{sym}(CuX) frequencies are less definite as the IR bands concerned are weak. In any case, this [and the $\delta(CuX_2)$ mode] may also involve a ν(CuP) component, and so its frequency is likely to be less directly dependent on the Cu–X bond strength than that of the ν_{asym}(CuX) mode. However, the trends in the vibrational frequencies of the CuX_2 units in $[CuX_2]^-$ and $[Cu(PPh_3)X_2]^-$ from X = Cl to X = I (Fig. 4) are very similar, and this provides additional support for the above assignments.

The dimer $[Cu_2(PPh_3)_2I_4]^{2-}$ shows a remarkably simple spectrum in the ν(CuI) region: a partially resolved doublet at 113 and 126 cm^{-1} (Fig. 3). This is surprising in view of the fact that the anion contains both terminal and bridging Cu–I bonds. In the case of the isostructural $[Hg_2(PPh_3)X_4]$ species, well separated bands due to the terminal and bridging ν(HgX) modes are observed.[33] However, the spectrum of $[NEt_4]_2[Cu_2I_4]$ is very similar in appearance to that of its PPh_3 adduct (Fig. 3). The $[Cu_2I_4]^{2-}$ ion also contains terminal and bridging Cu–I bonds (see above), and so might have been expected to give rise to well separated bands due to these two different Cu–I

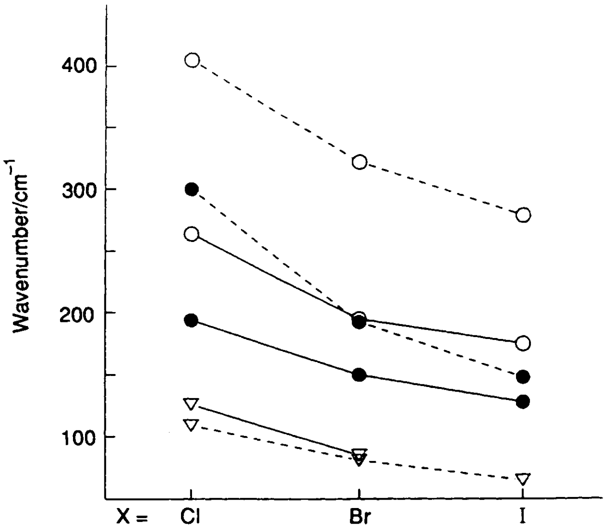


Fig. 4 Dependence on X of the wavenumbers of the ν_{asym}(CuX) (○), ν_{sym}(CuX) (●), and $\delta(CuX_2)$ (▽) modes of the CuX_2 units in $[CuX_2]^-$ (– – – – –) and $[Cu(PPh_3)X_2]^-$ (———)

Table 8 Comparison of copper–halogen vibrational bands (cm^{-1}) for $[CuX_2]^-$ and $[Cu(PPh_3)_nX_{3-n}]^{(2-n)-}$ (n = 0–2); X = Cl, Br or I

Complex	ν_{asym}(CuX)		ν_{sym}(CuX)	$\delta(CuX_2)$	Ref.
$[CuCl_2]^-$	405		300	109	31
$[Cu(PPh_3)_2Cl]$		298			32
$[Cu(PPh_3)Cl_2]^-$	264		194	126	*a*
$[CuCl_3]^{2-}$	—		—	—	
$[CuBr_2]^-$	322		193	81	31
$[Cu(PPh_3)_2Br]$		218			32
$[Cu(PPh_3)Br_2]^-$	195		150	85	*b,c*
$[CuBr_3]^{2-}$	185		—	—	14
$[CuI_2]^-$	279		148	65	31
$[Cu(PPh_3)_2I]$		184			32
$[Cu(PPh_3)I_2]^-$	175		128	—	*b*
$[CuI_3]^{2-}$	163		—	—	14

[a] This work, $[NEt_4]^+$ salt. [b] This work, $[NPr_4]^+$ salt. [c] Ref. 8, $[PPh_3Me]^+$ salt.

Table 9 Solid-state CP MAS ^{31}P NMR parameters for some triphenylphosphine copper(I) halide complexes[a]

Complex	δ	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	$\langle\Delta\nu_i\rangle$	$\Delta\nu_3/\Delta\nu_1$	Ref.
$[Cu(PPh_3)_2Cl]$	+4	0.94	1.27	1.43	1.21	1.52	19
$[Cu(PPh_3)Cl_2]^-$	−8	1.26	1.71	1.71	1.56	1.36	*b*
$[Cu(PPh_3)_2Br]$	+5	0.88	1.28	1.44	1.20	1.64	19
$[Cu(PPh_3)Br_2]^-$	−6	1.23	1.62	1.80	1.55	1.46	*b*
	−3	—	—	—	—	—	*c*
	−4	1.37	1.69	1.92	1.66	1.40	*d*
$[Cu(PPh_3)_2I]$	+5	0.88	1.20	1.43	1.17	1.63	19
$[Cu(PPh_3)I_2]^-$	−3	—	—	—	—	—	*c*
$[Cu_2(PPh_3)_2I_4]^{2-}$	−14	1.25	1.43	1.50	1.39	1.20	*b*
$[Cu_4(PPh_3)_4I_4]$ 'step'	+3	1.32	1.70	1.86	1.63	1.41	37
	−4	1.43	1.65	1.77	1.62	1.24	

[a] δ is the chemical shift in ppm relative to solid triphenylphosphine; $\Delta\nu_i$ (i = 1–3) are the splittings in kHz between adjacent lines in the quartet, i increasing from low to high field; $\langle\Delta\nu_i\rangle$ is the mean of the three $\Delta\nu_i$ values in kHz. [b] This work, $[NEt_4]^+$ salt. [c] This work, $[NPr_4]^+$ salt. [d] Ref. 8, $[PPh_3Me]^+$ salt.

bond types. One way of interpreting the unexpectedly simple spectrum observed in this case is to consider the $[Cu_2I_4]^{2-}$ ion as consisting of two trigonal CuI_3 units which share a pair of iodine atoms. A trigonal CuI_3 unit of D_{3h} symmetry would give rise to a single E′ ν(CuI) band in the IR spectrum. This band is observed at 163 cm^{-1} in the FIR spectrum of $[CuI_3]^{2-}$.[14] Such a vibration would also occur in $[Cu_2I_4]^{2-}$, but its two-fold degeneracy would be lifted by the lowering of symmetry which accompanies the linking of the CuI_3 units *via* the shared pair of iodine atoms, so that a splitting of this band would occur. This corresponds well with the observed spectrum of $[NEt_4]_2[Cu_2I_4]$ (Fig. 3), which shows a partially resolved doublet at almost the same frequency as that of the E′ ν(CuI) mode in $[CuI_3]^{2-}$. A similar relationship between the ν(PtX) bands in the IR spectra of $[PtX_4]^{2-}$ and $[Pt_2X_6]^{2-}$ has been noted previously.[34] The spectrum of $[Cu_2(PPh_3)_2I_4]^{2-}$ can be explained in the same way, the ν(CuI) bands being lowered in frequency relative to those for $[Cu_2I_4]^{2-}$ by a ratio similar to that involved in going from $[CuI_2]^-$ to $[Cu(PPh_3)I_2]^-$.

The relationship between the structures of $[Cu_2(PPh_2)_2I_4]^{2-}$ and the 'step' form of $[Cu_4(PPh_3)_4I_4]$ was discussed above, and this can be further explored in relation to the ν(CuI) frequencies. The 'step' form of $[Cu_4(PPh_3)_4I_4]$ shows IR bands at 162 and 109 cm^{-1} which were originally interpreted on the basis of the presence of both doubly- and triply-bridging iodine atoms in the structure.[35] Subsequent results for related systems suggested that it was the presence of both three- and four-co-ordinate copper which resulted in the two ν(CuX) bands.[8] This interpretation is supported by the present result for $[Cu_2(PPh_3)_2I_4]^{2-}$, which contains only four-co-ordinate copper, and which shows very nearly a single ν(CuI) band at a frequency close to that assigned to the four-co-ordinate copper in 'step' $[Cu_4(PPh_3)_4I_4]$.

CP MAS ^{31}P NMR Spectra.—These consist of asymmetric quartets due to coupling to the quadrupolar $^{63,65}Cu$ (nuclear spin $I = \frac{3}{2}$) nuclei.[6,36] The parameters measured from the spectra are listed in Table 9 together with those of a number of related complexes. The $\langle\Delta\nu_i\rangle$ are effectively the ^1J(CuP) coupling constants, and these show a marked increase from $[Cu(PPh_3)_2X]$ to $[Cu(PPh_3)X_2]^-$, in accordance with the generally observed trend of increasing coupling constant with decreasing number of co-ordinated PPh_3 molecules.[6] The ratio $\Delta\nu_3/\Delta\nu_1$ gives an indication of the magnitude of the quadrupole coupling constant at the copper nucleus; the divergence of this ratio from unity is approximately proportional to the copper nuclear quadrupole coupling constant.[6] The results in Table 9 therefore indicate that this coupling constant decreases from $[Cu(PPh_3)_2X]$ to $[Cu(PPh_3)X_2]^-$. This can be understood in terms of the lower σ-donor strength of X^- relative to PPh_3. The electric field gradient at the copper nucleus is determined primarily by the population of the copper 4p orbitals.[38] Replacement of a PPh_3 molecule by X^- results in a reduction in the population of these orbitals, and so in a reduction in the nuclear quadrupole coupling constant.

The spectra of $[NPr_4][Cu(PPh_3)X_2]$ contain very broad lines, and have the appearance of a quartet in which the outer pairs of lines have almost coalesced, so that no meaningful splitting parameters can be measured. These spectra are similar in appearance to that previously reported for $[Cu_2(PPh_3)_2I_3]^-$ in $[PPh_3Me][Cu_2(PPh_3)_2I_3]$.[9] For this latter compound it was suggested that the unusual nature of the spectrum might be related to the binuclear structure of the anion and the unusually short Cu ⋯ Cu distance which this involves. This now seems unlikely in view of the fact that similar spectra have been observed for the mononuclear complexes $[Cu(PPh_3)X_2]^-$. The fact that the observed distortion is associated with a broadening of the lines suggests that it may be due to a dynamic effect. The form of these spectra corresponds closely to that predicted for a spin $I = \frac{1}{2}$ nucleus coupled to an $I = \frac{3}{2}$ nucleus which is undergoing quadrupolar relaxation.[39,40] If this is the reason for the broadening and distortion of the spectra in the present cases this raises the question of why such relaxation normally has an insignificant effect on the solid-state ^{31}P NMR spectra of compounds which exhibit ^1J(Cu–P) coupling, but has a pronounced effect in a few cases. Further work, possibly involving variable-temperature studies, is required to resolve this question.

The parameters for $[Cu_2(PPh_3)_2I_4]^{2-}$ are compared in Table 9 with those for 'step' $[Cu_4(PPh_3)_4I_4]$, and these reflect the close structural relationship which exists between these two complexes. The spectrum of the tetramer consists of two quartets with significantly different $\Delta\nu_3/\Delta\nu_1$ ratios. The set of lines with the larger value of this ratio has been assigned to the trigonally co-ordinated copper atom, and the set with the lower ratio to the tetrahedrally co-ordinated copper atom, in accordance with the expected relative values of the copper nuclear quadrupole coupling constants for these sites.[37] This assignment is very well supported by the present result for $[Cu_2(PPh_3)_2I_4]^{2-}$, which contains tetrahedrally co-ordinated copper in an environment similar to that of the tetrahedrally co-ordinated copper in the 'step' tetramer, and which gives a single quartet with a $\Delta\nu_3/\Delta\nu_1$ ratio which is almost identical to that of the tetrahedral copper atom in the 'step' tetramer.

Acknowledgements

We acknowledge support of this work by grants from the New Zealand University Grants Committee, the University of Auckland Research Committee, and the Australian Research Grants Scheme. One of us (W. J.) gratefully acknowledges the grant of a period of study leave by the Inner Mongolia University. We thank David Camp and Kerry Penman for recording the solid-state NMR spectra.

References

1 B. J. Hathaway, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 533.
2 F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 115.
3 C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979.
4 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem.*, 1976, **15**, 1155.
5 P. C. Healy, C. Pakawatchai, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1905.
6 G. A. Bowmaker, J. D. Cotton, P. C. Healy, J. D. Kildea, S. B. Silong, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 1462.
7 S. Jagner and G. Helgesson, *Adv. Inorg. Chem.*, 1991, **37**, 1.
8 G. A. Bowmaker, B. W. Skelton, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1988, 2825.
9 G. A. Bowmaker, A. Camus, P. C. Healy, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 3883.
10 G. A. Bowmaker, A. Camus, R. D. Hart, J. D. Kildea, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1990, 3753.
11 G. A. Bowmaker, P. C. Healy, D. L. Kepert, J. D. Kildea, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1989, 1639.
12 G. A. Bowmaker, L. D. Brockliss, C. D. Earp and R. Whiting, *Aust. J. Chem.*, 1973, **26**, 2593.
13 G. A. Bowmaker, G. R. Clark and D. K. P. Yuen, *J. Chem. Soc., Dalton Trans.*, 1976, 2329.
14 G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus and N. Marsich, *J. Chem. Soc., Dalton Trans.*, 1984, 37.
15 G. A. Bowmaker, A. Camus, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1990, 727.
16 J. A. Ibers and W. C. Hamilton (Editors), *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
17 S. R. Hall and J. M. Stewart (Editors), *XTAL Users' Manual, Version 3.0*, Universities of Western Australia and Maryland, 1990.
18 J. C. Dyason, L. M. Engelhardt, P. C. Healy, H. L. Klich and A. H. White, *Aust. J. Chem.*, 1986, **39**, 2003.
19 G. A. Bowmaker, J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1089.
20 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1988, **42**, 691.
21 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1987, **41**, 230.
22 H. Hartl and I. Brüdgam, *Z. Naturforsch., Teil B*, 1989, **44**, 936.
23 J. C. Dyason, L. M. Engelhardt, C. Pakawatchai, P. C. Healy and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1243.
24 P. G. Eller, G. J. Kubas and R. R. Ryan, *Inorg. Chem.*, 1977, **16**, 2454.
25 M. R. Churchill, B. G. De Boer and D. J. Donovan, *Inorg. Chem.*, 1975, **14**, 617.
26 M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand., Ser. A*, 1982, **36**, 751.
27 M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 411.
28 H. Hartl, I. Brüdgam and F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B*, 1985, **40**, 1032; M. Asplund and S. Jagner, *Acta Chem. Scand., Ser. A*, 1984, **38**, 297.
29 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta*, 1980, **43**, 87.
30 N. A. Bell, L. A. March and I. W. Nowell, *Inorg. Chim. Acta*, 1989, **156**, 201.
31 D. N. Waters and B. Basak, *J. Chem. Soc. A*, 1971, 2733.
32 G. A. Bowmaker, P. C. Healy, J. D. Kildea and A. H. White, *Spectrochim. Acta, Part A*, 1988, **44**, 1219.
33 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta*, 1983, **69**, 155.
34 P. L. Goggin, *J. Chem. Soc., Dalton Trans.*, 1974, 1483; P. L. Goggin and J. Mink, *Inorg. Chim. Acta*, 1978, **26**, 119.
35 B.-K. Teo and D. M. Barnes, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 681.
36 E. M. Menger and W. S. Veeman, *J. Magn. Reson.*, 1982, **46**, 257.
37 J. C. Dyason, P. C. Healy, L. M. Engelhardt, C. Pakawatchai, V. A. Patrick, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 831.
38 G. A. Bowmaker, P. D. W. Boyd and R. J. Sorrenson, *J. Chem. Soc., Faraday Trans. 2*, 1985, 1627.
39 J. Bacon, R. J. Gillespie and J. W. Quail, *Can. J. Chem.*, 1963, **41**, 3063.
40 A. Marker and M. J. Gunter, *J. Magn. Reson.*, 1982, **47**, 118.

Received 22nd *July* 1991; *Paper* 1/03728E