Structural and Spectroscopic Characterization of Complexes containing the Mononuclear Trihalogenometalates $[CuI_3]^{2-}$, $[CuBr_3]^{2-}$, and $[AgI_3]^{2-}$. Crystal structure of $[PMePh_3]_2[CuI_3]$ †

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The new compounds $[PMePh_3]_2[CuI_3]$, $[AsMePh_3]_2[CuI_3]$, $[PMePh_3]_2[CuBr_3]$, and $[PMePh_3]_2[AgI_3]$ have been prepared. Unlike previously reported compounds of stoicheiometry $[cation]_2[MX_3]$ (M = Cu^I or Ag^I) which contain infinite polymeric anions with bridging halide ions and tetrahedrally co-ordinated metal atoms, the present compounds contain mononuclear $[MX_3]^{2-}$ ions with essentially trigonal planar co-ordination of the metal atoms. This has been verified in the case of $[PMePh_3]_2[CuI_3]$ by conventional *X*-ray diffraction techniques. Crystals are Monoclinic of space group $P2_1$ with a = 9.580(1), b = 12.476(2), c = 16.410(1), and Z = 2. The $[CuI_3]^{2-}$ anion in this compound is not perfectly symmetrical, as the Cu atom is displaced by 0.015(1) Å from the plane of the three iodine atoms and the Cu–I bond lengths show significant differences. The far-i.r. spectra of these compounds show a strong band at 163, $[CuI_3]^{2-}$, 133, $[AgI_3]^{2-}$, or 190 cm^{-1}, $[CuBr_3]^{2-}$, which can be assigned to the antisymmetric metal–halogen stretching mode of the $[MX_3]^{2-}$ units. Approximate normal co-ordinate calculations yield metal–halogen force constants for $[MX_3]^{2-}$ which, as expected, are lower than those for the corresponding $[MX_2]^-$ species. ^{127}I nuclear quadrupole resonance measurements on $[PMePh_3]_2[MI_3]$ (M = Cu^I or Ag^I) show the presence of three crystallographically inequivalent iodine atoms. The ^{63}Cu and ^{65}Cu n.q.r. frequencies in the copper complex are almost identical to those found previously in other complexes containing copper(I) bound to three equivalent ligands in a trigonal planar environment. $[PMePh_3]_2[CuBr_3]$ can be prepared in a second isomeric form. This is shown by means of vibrational spectroscopy, and copper and bromine n.q.r. spectroscopy, to contain non-interacting $[CuBr_2]^-$ and Br^- ions, and is therefore formulated as $[PMePh_3]_2[CuBr_2]Br$. Attempts to prepare complexes containing $[MX_3]^{2-}$ ions with cations such as $[NEt_4]^+$, $[NPr_4]^+$, $[AsPh_4]^+$, and $[N(PPh_3)_2]^+$ resulted either in the formation of complexes of different stoicheiometry or compounds of the desired stoicheiometry which, however, do not appear to contain mononuclear, planar $[MX_3]^{2-}$ species.

Examples of trigonal co-ordination for the monovalent Group 1B metals are rather rare. A few cases of mononuclear trigonal complexes of Cu^I and Ag^I have been reported,[1–3] and further examples of trigonal co-ordination occur in some multinuclear complexes of these metals.[3–6] The simplest example of a mononuclear trigonal complex which has been fully characterized structurally is the $[Cu(CN)_3]^{2-}$ ion in $Na_2[Cu(CN)_3]\cdot 3H_2O$.[1] The vibrational and u.v.–visible absorption spectra of this species have also been reported.[7,8] Of equally fundamental interest are the halogeno-complexes $[MX_3]^{2-}$, whose existence in solutions of the metal–halides in halide media has previously been proposed. Formation constants for these species have been determined from solubility studies,[9] or from u.v.–visible absorption data.[10] However, in contrast to the situation for the corrresponding $[MX_2]^-$ complexes,[11,12] these species have not been more definitely characterized structurally or spectroscopically.

Several solid complexes of the type $[cation]_2[MX_3]$ (M = Cu^I or Ag^I) are known, but the only complexes of this type for which crystal structures have been determined to date contain infinite polymeric anions made up of linked MX_4 tetrahedra.[13–15]

In the present work we have found that solid complexes containing isolated $[MX_3]^{2-}$ ions can be obtained using the counter ion $[PMePh_3]^+$ (and in one case $[AsMePh_3]^+$). We describe herein the characterization of such complexes by means of *X*-ray crystallography, vibrational spectroscopy, and nuclear quadrupole resonance (n.q.r.) spectroscopy.

Experimental

Preparation of Compounds.—Copper(I) chloride and bromide were prepared by the method of Keller and Wycoff [16] and used immediately. Bis(triphenylphosphine)iminium chloride dichloromethane, $[N(PPh_3)_2]Cl\cdot CH_2Cl_2$,[17] and methyltriphenylphosphonium chloride [18] were prepared by literature methods. Methyltriphenylphosphonium-iodide and -bromide were prepared by adding stoicheiometric amounts of iodomethane or bromomethane to a benzene solution of triphenylphosphine. The white solids so formed were recrystallized from absolute ethanol–diethyl ether. Tetraphenylphosphonium bromide was prepared by the method of Chatt and Mann.[19] Methyltriphenylarsonium iodide was prepared by adding iodomethane in stoicheiometric quantity to a solution of triphenylarsine in benzene. The product was recrystallized from absolute ethanol–diethyl ether. Silver bromide and silver iodide were prepared by precipitation from an aqueous silver nitrate solution with the appropriate sodium salt. They were filtered off, washed with absolute ethanol and diethyl ether and dried *in vacuo* before use.

Triphenylphosphine (Merck), triphenylarsine (Fluka), tetraphenylarsonium chloride monohydrate (Riedel-de-Häen), silver chloride (B.D.H.), copper(I) iodide (Riedel-de-Häen), tetrapropylammonium iodide (Fluka), tetrapropylammonium bromide (Eastman), and tetraethylammonium chloride

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† Bis(methyltriphenylphosphonium) tri-iodocuprate(I).

Supplementary data available (No. SUP 23739, 16 pp.): structure factors, thermal parameters, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

(Aldrich) were obtained commercially and used without further purification.

Peroxide-free diethyl ether was obtained by first drying the ether on an alumina column and standing over sodium metal. The ether was then refluxed with sodium and benzophenone.

Bis(methyltriphenylphosphonium) hexaiodotetracuprate(I). This complex was prepared by the literature method.[4]

Bis(methyltriphenylphosphonium) tri-iodocuprate(I), $[PMePh_3]_2[CuI_3]$. A quantity of $[PMePh_3]I$ (8.90 g, 22.02 mmol) was suspended in degassed acetone (100 cm^3) under dinitrogen with stirring. To this was added copper(I) iodide (1.91 g, 10.01 mmol). A clear solution resulted and then a white solid formed on stirring. This was dissolved by heating for 30 min and the solution then allowed to regain room temperature. The pale lemon needles which formed were filtered off and dried *in vacuo*. Yield 7.81 g (78.1%), m.p. 160—161 °C.

Methyltriphenylarsonium tetraiodotricuprate(I), $[AsMePh_3][Cu_3I_4]$. $[AsMePh_3]I$ (0.94 g, 2.1 mmol) and copper(I) iodide (0.20 g, 1.05 mmol) were dissolved in nitromethane (5 cm^3) giving a pale yellow solution, from which the complex precipitated spontaneously or by addition of ligroin, m.p. 167—168 °C. Yellow needles of $[AsMePh_3]_2[Cu_4I_6]$[4] post-precipitated from the mother-liquor.

Bis(methyltriphenylarsonium) tri-iodocuprate(I), $[AsMePh_3]_2[CuI_3]$. This compound was obtained as a side-product in the preparation of $[AsMePh_3][Cu_3I_4(AsPh_3)_3]$ and was recrystallized from acetone–diethyl ether, m.p. 154—155 °C. When 1 : 2 ratios of CuI to $[AsMePh_3]I$ were reacted in acetone, $[AsMePh_3]_2[Cu_4I_6]$ and $[AsMePh_3][Cu_3I_4]$ were obtained. When $[AsMePh_3]I$, CuI, and $AsPh_3$ in 1 : 1 : 1 ratio were reacted in CH_2Cl_2, $[AsMePh_3][Cu_3I_4(AsPh_3)_3]$, m.p. 195—196 °C (Found: C, 44.3; H, 3.4; Cu, 9.9; I, 26.3. Calc. for $C_{73}H_{48}As_4Cu_3I_4$: C, 45.2; H, 3.3; Cu, 9.8; I, 26.2%) was formed in low yield. On adding diethyl ether to the mother-liquor, $[AsMePh_3]_2[CuI_3]$ was obtained.

Bis(methyltriphenylphosphonium) tri-iodoargentate(I), $[PMePh_3]_2[AgI_3]$. Silver iodide (0.45 g, 1.92 mmol) and $[PMePh_3]I$ (1.55 g, 3.83 mmol) were dissolved in acetonitrile (50 cm^3) by stirring in the dark for 2 h. The resulting clear solution was filtered and evaporated to 5 cm^3 by heating. On cooling, white needles formed which were filtered off and dried *in vacuo*. Yield 1.23 g (61.5%), m.p. 176—178 °C.

Bis(methyltriphenylphosphonium) tribromocuprate(I), $[PMePh_3]_2[CuBr_3]$, *and bis(methyltriphenylphosphonium) dibromocuprate*(I) *bromide*, $[PMePh_3]_2[CuBr_2]Br$. Copper(I) bromide (0.23 g, 1.6 mmol) and $[PMePh_3]Br$ (1.62 g, 4.5 mmol) were dissolved in deaerated absolute ethanol (20 cm^3) by heating and stirring under dinitrogen. To the resulting clear solution was added diethyl ether (40 cm^3). The white solid which formed was washed once with 5 cm^3 of a 1 : 2 EtOH–Et_2O mixture, and twice with 5-cm^3 portions of Et_2O. This preparation yields one or other of two different products with the same stoicheiometry (2 mol of $[PMePh_3]Br$ to 1 mol of CuBr): compound (1), yield 1.09 g (79%), m.p. 139—140 °C; compound (2), yield 1.17 g (85%), m.p. 152—153 °C. It was not possible to determine unique conditions under which one or other of these products forms, but both have been reproducibly prepared on many occasions under apparently identical conditions. The far-i.r. spectra of these compounds (see Results and Discussion section) show that (1) contains $[CuBr_3]^{2-}$ ions, and is therefore formulated as $[PMePh_3]_2[CuBr_3]$ while (2) contains non-interacting $[CuBr_2]^-$ and Br^- ions, and is best formulated as $[PMePh_3]_2[CuBr_2]Br$. These compounds also show significant differences in the positions and intensities of cation bands in their i.r. spectra (4 000—400 cm^{-1}). For example, a strong doublet which appears at 903, 919 cm^{-1} in $[PMePh_3]Br$ occurs at 887, 880 cm^{-1} in $[PMePh_3]_2[CuBr_3]$ and at 910—915 cm^{-1} in $[PMePh_3]_2[CuBr_2]Br$.

Methyltriphenylphosphonium dibromocuprate(I), $[PMePh_3][CuBr_2]$. Copper(I) bromide (0.72 g, 5.0 mmol) was added with stirring to a deaerated solution of $[PMePh_3]Br$ (1.79 g, 5.0 mmol) in acetone (30 cm^3). Stirring was continued for 30 min and diethyl ether (30 cm^3) added to the resulting clear solution. The white solid which formed [yield 2.1 g (84%)] was collected and recrystallized from acetone (microcrystalline powder) or CH_2Cl_2–Et_2O (needles), m.p. 107—108 °C.

Tris(methyltriphenylphosphonium) tetrabromoargentate(I), $[PMePh_3]_3[AgBr_4]$. Silver bromide (0.42 g, 2.22 mmol) and $[PMePh_3]Br$ (1.58 g, 4.43 mmol) were dissolved in acetonitrile (50 cm^3) by stirring and heating for 30 min. The solution was reduced in volume to 15 cm^3 and then filtered. On cooling a white powder formed which was filtered off and dried *in vacuo*, m.p. 185—188 °C.

Methyltriphenylphosphonium dichlorocuprate(I), $[PMePh_3][CuCl_2]$. To degassed acetone (35 cm^3) were added under nitrogen, copper(I) chloride (0.32 g, 3.19 mmol) and $[PMePh_3]Cl$ (2.00 g, 6.39 mmol). This suspension was stirred and heated and absolute ethanol (5 cm^3) added. Stirring and heating were continued until all solid had dissolved. The solution was then allowed to regain room temperature, filtered, and reduced in volume until white needles formed which were filtered off, recrystallized from acetone and absolute ethanol, and dried *in vacuo*, m.p. 141—145 °C.

Tetraphenylphosphonium dibromoargentate(I), $[PPh_4][AgBr_2]$. $[PPh_4]Br$ (2.40 g, 5.72 mmol) and silver bromide (0.60 g, 3.21 mmol) were dissolved in acetonitrile (25 cm^3) by heating. The resulting clear solution was filtered, and on cooling white needles formed which were filtered off and dried *in vacuo*, m.p. 218—220 °C.

Tris(tetraphenylarsonium) pentachlorodiargentate(I), $[AsPh_4]_3[Ag_2Cl_5]$. $[AsPh_4]Cl{\cdot}H_2O$ (1.34 g, 3.06 mmol) and silver chloride (0.22 g, 1.53 mmol) were dissolved in acetonitrile (15 cm^3) by heating in the dark. The volume of the resulting clear solution was then reduced to 3 cm^3 and on standing, short white needles formed which were filtered off and dried *in vacuo*, m.p. 172—174 °C.

Tetraethylammonium trichlorodiargentate(I), $[NEt_4][Ag_2Cl_3]$. $[NEt_4]Cl$ (1.40 g, 8.43 mmol) and silver chloride (0.60 g, 4.21 mmol) were dissolved in acetonitrile (25 cm^3) by heating in the dark. The volume was reduced to 10 cm^3, the solution filtered, and on cooling white needles formed which were filtered off, recrystallized from acetonitrile, and dried *in vacuo*, m.p. 203—206 °C.

Tris(tetrapropylammonium) tetrabromoargentate(I), $[NPr_4]_3[AgBr_4]$. Silver bromide (0.52 g, 2.78 mmol) and $[NPr_4]Br$ (1.48 g, 5.55 mmol) were dissolved in acetonitrile (50 cm^3) by stirring for 30 min. The volume was reduced to 15 cm^3, the solution filtered, and on cooling a white powder formed which was filtered off and dried *in vacuo*, m.p. 110—112 °C.

Bis(tetrapropylammonium) tri-iodoargentate(I), $[NPr_4]_2[AgI_3]$. $[NPr_4]I$ (2.18 g, 6.97 mmol) was dissolved in acetonitrile (50 cm^3). To this was added silver iodide (0.82 g, 3.48 mmol) and the solution stirred in the dark for 30 min. The white solid which formed on evaporating to dryness was recrystallized from acetonitrile and dried *in vacuo*, m.p. 133—137 °C.

Bis(triphenylphosphine)iminium dichloroargentate(I), $[N(PPh_3)_2][AgCl_2]$. The salt $[N(PPh_3)_2]Cl{\cdot}CH_2Cl_2$ (1.50 g, 2.28 mmol) and silver chloride (0.16 g, 1.14 mmol) were dissolved in acetonitrile (25 cm^3) by heating in the dark. The resulting clear solution was reduced to 5 cm^3 in volume, filtered, and on standing white crystals formed. These were filtered off, recrystallized from acetonitrile and dried *in vacuo*, m.p. 229—231 °C.

Table 1. Elemental analyses and conductivity [a]

Compound	Calculated (%)						Found (%)						Conductivity/ S cm^2 mol^{-1}
	C	H	N	Cu	X	P	C	H	N	Cu	X	P	
$[PMePh_3]_2[CuI_3]$	45.7	3.6	—	6.4	38.1	6.2	45.2	3.7	—	6.4	38.6	6.3	56.0 [b] 176.7
$[AsMePh_3]_2[CuI_3]$	42.0	3.3	—	5.9	35.0	—	41.9	3.3	—	5.9	35.3	—	55.5 [b] 170.3
$[AsMePh_3][Cu_3I_4]$	22.4	1.8	—	18.7	49.8	—	23.2	1.7	—	18.9	49.3	—	—
$[PMePh_3]_2[AgI_3]$	43.8	3.5	—	—	—	—	43.8	3.8	—	—	—	—	178.9
$[PMePh_3]_2[CuBr_3]$	53.2	4.2	—	7.4	27.9	7.2	52.6	4.1	—	7.3	27.9	7.0	50.8 [b]
$[PMePh_3]_2[CuBr_2]Br$	53.2	4.2	—	—	27.9	—	53.6	4.5	—	—	27.6	—	159.0
$[PMePh_3][CuBr_2]$	45.6	3.6	—	12.7	31.9	6.2	45.5	3.4	—	12.6	32.0	6.2	34.0 [b]
$[PMePh_3]_3[AgBr_4]$	54.4	4.3	—	—	—	—	53.9	4.6	—	—	—	—	236.4
$[PMePh_3][CuCl_2]$	55.4	4.4	—	—	17.2	—	55.3	4.7	—	—	17.4	—	—
$[NEt_4][Ag_2Cl_3]$	21.2	4.5	3.1	—	—	—	22.0	5.0	3.5	—	—	—	137.1
$[NPr_4]_3[AgBr_4]$	43.8	8.6	4.3	—	—	—	42.9	8.8	4.3	—	—	—	244.2
$[NPr_4]_2[AgI_3]$	33.5	6.6	3.2	—	—	—	33.5	6.5	3.1	—	—	—	168.8
$[AsPh_4]_3[Ag_2Cl_5]$	56.0	3.9	—	—	—	—	54.9	4.1	—	—	—	—	218.7
$[PPh_4][AgBr_2]$	47.5	3.3	—	—	—	—	48.1	3.5	—	—	—	—	88.9
$[N(PPh_3)_2][AgCl_2]$	60.3	4.3	2.0	—	—	—	59.6	4.5	2.1	—	—	—	82.0

[a] 10^{-3} mol dm^{-3} solutions, nitromethane, 25 °C, unless otherwise stated. [b] 10^{-3} mol dm^{-3} solutions, 1,2-dichloroethane solvent, 20 °C.

Microanalyses.—These measurements were carried out by Professor A. D. Campbell at the University of Otago, Dunedin, New Zealand.

Conductivity Measurements.—Conductivity measurements were carried out using a Beckman RC-18A conductivity bridge.

Spectroscopy.—Far-i.r. spectra (50—400 cm^{-1}) were obtained on a Grubb-Parsons Cube MKII interferometer fitted with a 6.25-μm Mylar-film beam splitter. They were run on petroleum jelly mulls between Polythene plates, and calibrated by using the spectrum of water vapour. Far-i.r. spectra were also run at *ca.* 125 K in a Grubb-Parsons GMR 01 low-temperature cell cooled with liquid nitrogen. Spectra were Fourier transformed and printed using an interfaced CBM microcomputing system.

Raman spectra were obtained on a Jasco R300 Raman spectrometer and were excited with a Coherent CR4 argon-ion laser (514.5 or 488.0 nm), with powers between 20 and 50 mW. The spectra were run on polycrystalline samples in glass capillary tubes.

N.q.r. spectra were obtained at the University of Tasmania or at the Technical University of Munich on a Wilks NQR-IA spectrometer, and the frequencies were measured with a Hewlett-Packard model 5345 A frequency meter or a Nelson Ross Plugin Spectrum Analyser.

X-*Ray Crystal Structure of* $[PMePh_3]_2[CuI_3]$.—Preliminary *X*-ray photographs of the pale lemon crystals showed monoclinic diffraction symmetry, with systematically absent reflections ($0\ k\ 0$, $k = 2n + 1$) corresponding to space group $P2_1$ (no. 4). The crystals are short needles, elongated along the *b* axial direction. The crystal selected for data collection was bounded by faces (1 0 0), ($\bar{1}$ 0 0), (0 0 1), (0 0 $\bar{1}$), (0 $\bar{1}$ 1), (0 $\bar{1}$ 1), and (0 1 0), and of dimensions 0.40 × 0.18 × 0.12 mm. Unit-cell dimensions were derived from a least-squares fit to the setting angles of 25 reflections on a Nonius CAD-4 diffractometer.

Crystal data. $C_{38}H_{36}CuI_3P_2$, $M = 998.91$, Monoclinic, $a = 9.580(1)$, $b = 12.476(2)$, $c = 16.410(1)$ Å, $\beta = 102.71(1)°$, $U = 1\,913.1(7)$ Å^3, $F(000) = 964$, $D_m = 1.73(1)$ (by flotation in CCl_4–1,2-dibromoethane), $Z = 2$, $D_c = 1.73$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.7107$ Å, Zr filter, μ(Mo-K_α) = 31.48 cm^{-1}, $T = 291 \pm 1$ K.

Intensity data were collected to the practical crystal limit of $\theta = 27°$, and processed in the normal manner (for the absorption corrections the range of transmission coefficients was 0.710—0.573 *). After averaging equivalent measurements the data set consisted of 2 261 unique observed reflections for which $I > 3\sigma(I)$.

Structure determination and refinement. The structure was solved by locating the iodine and copper atoms from a Patterson function, and the remaining non-hydrogen atoms from a subsequent ' difference ' electron-density map. The origin was fixed by setting the *y* co-ordinate of I(1) to 0.0. The atomic arrangement established the space group as $P2_1$ rather than the alternative possibility of $P2_1/m$. Refinement of atomic parameters was by full-matrix least squares, minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4|F_o|^2/\sigma^2(F_o^2)$. Initially, isotropic thermal parameters were employed, but after two cycles the iodine, copper, and phosphorus atoms were assigned anisotropic values. No attempt was made to locate hydrogen atoms nor to refine the carbon atoms anisotropically as this was not considered warranted. In the final four least-squares cycles an extinction parameter was refined. † All parameter shifts were then small (maximum positional shift/error 0.24) and refinement was terminated with $R = 0.034$ and $R' \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.046$. No peak in a final ' difference ' electron-density map exceeded 0.3 e Å^{-3}. Refinement was also carried out with opposite polar axis direction, but the residual was slightly higher, and the anion geometry did not become more symmetric.

Results and Discussion

The complexes studied in this work were prepared by dissolution of the metal(I) halide in a solution of the appropriate ammonium, phosphonium, or arsonium halide (see Experimental section). Analytical data for the complexes prepared are given in Table 1.

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* All computing was carried out using the SDP suite of programs on a PDP-11 computer.

† The refined value of the extinction parameter *g* was 1.252×10^{-8}. The expression used was $|F_c| = |F_o|(1 + gI_c)$.

Table 2. Atomic positions for $[PMePh_3]_2[CuI_3]$

Atom	*x*	*y*	*z*
I(1)	0.245 65(8)	0.000 00	0.184 14(5)
I(2)	−0.095 42(8)	−0.134 89(9)	0.304 69(5)
I(3)	0.220 25(10)	−0.346 69(9)	0.237 88(5)
Cu	0.123 4(2)	−0.157 8(1)	0.240 73(9)
P(1)	0.437 2(3)	0.473 3(3)	0.522 1(2)
P(2)	0.563 5(3)	0.708 4(3)	0.063 5(2)
C(1)	0.480(1)	0.385(1)	0.610 9(8)
C(2)	0.339(1)	0.589(1)	0.546 4(7)
C(3)	0.280(1)	0.658(1)	0.482 3(7)
C(4)	0.202(2)	0.748(1)	0.499 3(9)
C(5)	0.190(2)	0.770(2)	0.581 3(11)
C(6)	0.251(2)	0.699(2)	0.644 5(11)
C(7)	0.327(2)	0.605(1)	0.628 0(9)
C(8)	0.597(1)	0.522(1)	0.497 7(7)
C(9)	0.728(1)	0.522(1)	0.555 6(8)
C(10)	0.847(2)	0.570(1)	0.538 4(10)
C(11)	0.844(2)	0.617(1)	0.459 9(9)
C(12)	0.716(2)	0.617(1)	0.401 2(9)
C(13)	0.588(1)	0.571(1)	0.419 1(8)
C(14)	0.334(1)	0.405(1)	0.433 5(8)
C(15)	0.406(2)	0.332(1)	0.389 8(10)
C(16)	0.330(2)	0.274(2)	0.322 3(11)
C(17)	0.185(2)	0.287(1)	0.297 2(10)
C(18)	0.113(2)	0.362(2)	0.335 6(12)
C(19)	0.187(2)	0.418(1)	0.406 4(11)
C(20)	0.517(1)	0.794(1)	0.141 9(8)
C(21)	0.401(1)	0.669(1)	−0.011 5(6)
C(22)	0.270(1)	0.692(1)	0.004 1(7)
C(23)	0.147(1)	0.653(1)	−0.055 2(9)
C(24)	0.164(2)	0.596(1)	−0.124 4(9)
C(25)	0.298(1)	0.575(1)	−0.136 9(8)
C(26)	0.420(1)	0.612(1)	−0.080 6(8)
C(27)	0.650(1)	0.590(1)	0.109 6(7)
C(28)	0.616(1)	0.551(1)	0.180 9(8)
C(29)	0.675(2)	0.454(1)	0.212 1(9)
C(30)	0.765(2)	0.396(1)	0.175 6(10)
C(31)	0.795(2)	0.435(1)	0.101 6(9)
C(32)	0.737(1)	0.533(1)	0.068 5(8)
C(33)	0.678(1)	0.781(1)	0.010 2(7)
C(34)	0.627(2)	0.835(1)	−0.059 8(9)
C(35)	0.713(2)	0.903(1)	−0.098 2(10)
C(36)	0.854(1)	0.914(1)	−0.058 1(8)
C(37)	0.909(1)	0.865(1)	0.015 4(8)
C(38)	0.825(1)	0.795(1)	0.051 5(8)

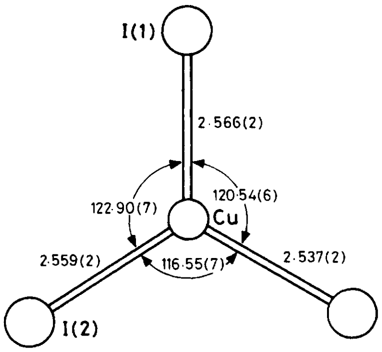

Figure 1. Geometry of $[CuI_3]^{2-}$ in $[PMePh_3]_2[CuI_3]$; distances in Å, angles in degrees

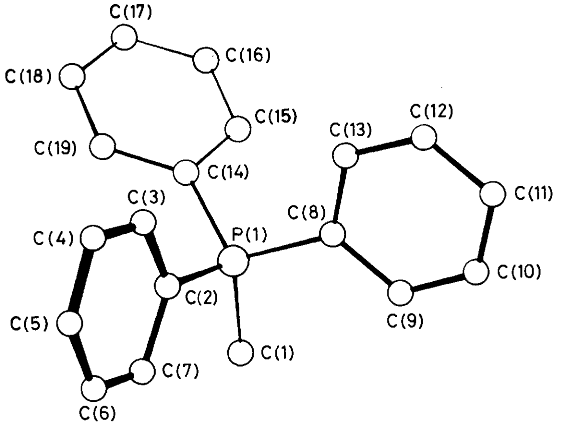

Figure 2. The phosphonium ion numbering scheme in $[PMePh_3]_2$-$[CuI_3]$. Only cation (1) is shown. For cation (2) use P(2) and add 19 to the corresponding carbon atom numbers of cation (1)

The compounds $[PMePh_3]_2[MI_3]$ (M = Cu^I or Ag^I) were prepared from solutions in which the ratio I^- : MI was approximately 2 : 1. Two distinct compounds of stoicheiometry $[PMePh_3]_2[CuBr_3]$ were obtained from solutions with a Br^- : CuBr ratio of 3 : 1. Attempts to prepare the corresponding chloro-complex led only to the isolation of $[PMePh_3]$-$[CuCl_2]$ for Cl^- : CuCl ratios up to 10 : 1. The corresponding bromo-complex, $[PMePh_3][CuBr_2]$, was obtained from a 1 : 1 Br^- : CuBr reaction mixture. $[PMePh_3]_3[AgBr_4]$ was obtained from a 2 : 1 Br^-: AgBr reaction mixture. $[AsMePh_3]_2[CuI_3]$ was obtained only as a by-product in the preparation of other complexes (see Experimental section). When the preparation of this complex from 2 : 1 I^- : CuI reaction mixtures was attempted, only the complexes $[AsMePh_3]_2[Cu_4I_6]$ (previously reported [4]) and $[AsMePh_3][Cu_3I_4]$ were obtained.

There is clearly no systematic method of preparing halogenometalate complexes of this type with any desired stoicheiometry. The stoicheiometry and the structures of the resulting solids depend strongly on the nature of the cation and on the preparative conditions (solvent, mol ratio of reagents, *etc.*) employed. The most significant result of the present work is that a number of solids containing discrete $[MX_3]^{2-}$ ions have been prepared for the first time. The conductivities of the $[cation]_2[MX_3]$ complexes in solution (Table 1) suggest that these behave as 2 : 1 electrolytes.[20]

Information about the structure of the anions in these compounds was obtained in the first instance from their vibrational spectra and, in some cases, their n.q.r. spectra. These will be discussed later. In the case of $[PMePh_3]_2[CuI_3]$ a crystal structure analysis was carried out to check the conclusions based on the spectroscopic results. This will be discussed first, since it provides a reference point against which the structures of the other compounds can be discussed.

Crystal Structure of $[PMePh_3]_2[CuI_3]$.—Positional atomic co-ordinates are listed in Table 2. Bond lengths and bond angles in the anion are shown in Figure 1. The atomic-numbering scheme is shown in Figures 1 and 2. *X*-Ray analysis shows that the crystals are ionic, and confirms the existence of the mononuclear $[CuI_3]^{2-}$ ion. Electrical neutrality is maintained by the presence of two methyltriphenylphosphonium cations.

(*a*) $[PMePh_3]^+$. In most respects the geometries of the crystallographically independent $[PMePh_3]^+$ ions are normal. The average of the eight P–C distances is 1.797 Å (1.774—1.832 Å), the average C–P–C angle is 109.5° (106.9—110.8°), the phenyl rings are planar, and the phosphorus atoms are displaced from the planes of the phenyl rings by no more than 0.2 Å. The P–C(methyl) distances are not distinguishable from the P–C(phenyl) distances. However, the phenyl rings are not symmetrically aligned with respect to the methyl–P bond

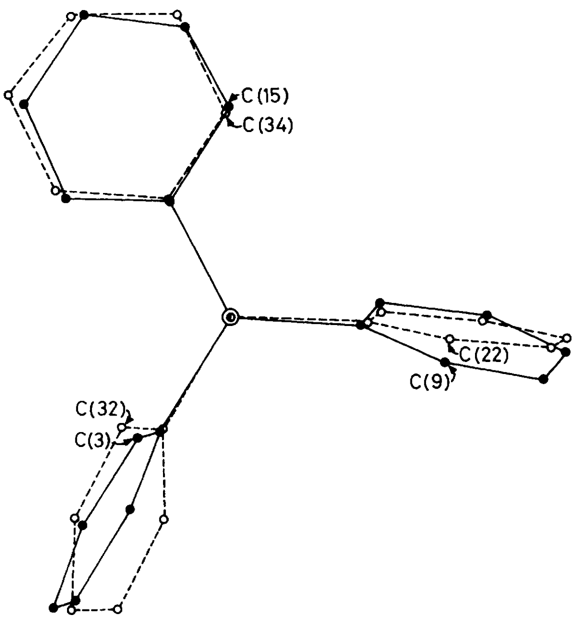

Figure 3. Projection of the cations perpendicular to the methyl–phosphorus bonds in [PMePh$_3$]$_2$[CuI$_3$]

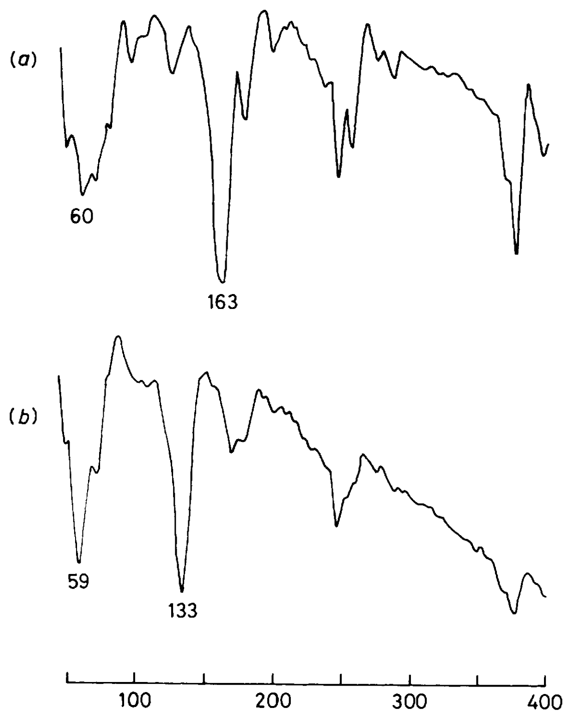

Figure 4. Far-i.r. spectra (at *ca.* 125 K) of (*a*) [PMePh$_3$]$_2$[CuI$_3$] and (*b*) [PMePh$_3$]$_2$[AgI$_3$]

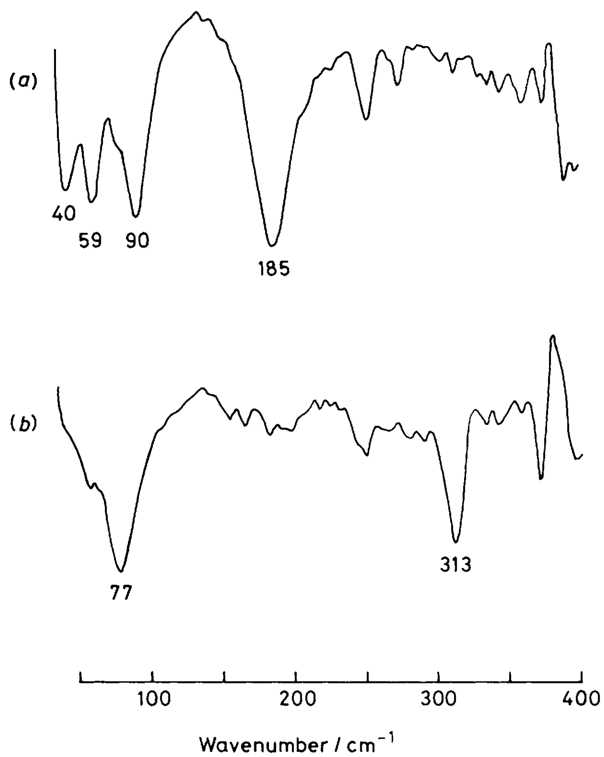

Figure 5. Far-i.r. spectra (at *ca.* 300 K) of (*a*) [PMePh$_3$]$_2$[CuBr$_3$] and (*b*) [PMePh$_3$]$_2$[CuBr$_2$]Br

direction. Instead of adopting a regular ' propeller blade ' orientation, the phenyl rings are disposed such that the plane of one ring in each cation lies almost perpendicular to the methyl–P line, one is nearly parallel, and the remaining ring adopts an intermediate orientation. These geometries are illustrated in Figure 3, which gives superimposed projections as seen down the methyl–P line. The irregular nature of the ring orientation is clearly seen in the displacements of C(1) or C(20) from the appropriate phenyl ring planes. It is not clear why the cations adopt their particular unsymmetrical geometries. Crystal-packing forces are frequently invoked to explain such effects, and a calculation of intermolecular distances shows that three cation–cation contacts are shorter than 3.6 Å [C(22)–C(31′) 3.48, C(23)–C(36″) 3.53, C(24)–C(37″) 3.54 Å],* but none of the cation–anion interactions is particularly short (see later).

(*b*) [CuI$_3$]$^{2-}$. The [CuI$_3$]$^{2-}$ ion has a planar triangular geometry with each iodine atom being bonded to the central trigonally-co-ordinated copper atom (Figure 1). The ion does not possess strict three-fold symmetry in the solid state in that the Cu–I bond lengths and I–Cu–I bond angles are not all equivalent. The I ··· I non-bonded distances of 4.502, 4.431, and 4.334 Å for I(1) ··· I(2), I(1) ··· I(3), and I(2) ··· I(3), respectively also indicate the extent of the asymmetry. The copper atom is displaced by 0.015(1) Å from the plane defined by the three iodine atoms ($-0.4076X - 0.1383Y - 0.9026Z + 3.3489 = 0$). The packing of the ions into the unit cell is such that there are far more cation–cation than cation–anion contacts. The nearest contact to the [CuI$_3$]$^{2-}$ ion is C(38) at a distance of 3.78 Å, and there are five other contacts shorter than 4.0 Å. None of these contacts is considered sufficiently short to influence greatly the geometry of [CuI$_3$]$^{2-}$ but their combined influence cannot be discounted from causing the small distortions from ideality.

Vibrational Spectra.—Selected far-i.r. spectra are shown in Figures 4 and 5 and the wavenumbers of bands assigned to the anions are given in Table 3.

For an [MX$_3$]$^{2-}$ ion of D_{3h} symmetry, the symmetry and

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* A prime denotes an atom at $1 - x, \frac{1}{2} + y, -z$; double primes denote those at $1 - x, -\frac{1}{2} + y, -z$.

Table 3. Low-frequency vibrational spectra (cm^{-1})

Compound	I.r. (*ca.* 120 K)	Raman (*ca.* 300 K)	Assignment
$[PMePh_3]_2[CuI_3]$	163s	172w, 167w, 152vw	ν(Cu–I) E'
	80w, 69m, 60m, 48m	80s br, 59 (sh), 49m	$[CuI_3]^{2-}$ bending
$[AsMePh_3]_2[CuI_3]$	165 (sh), 157s	177w, 161w	ν(Cu–I) E'
		149w, 131w, 110 (sh)	unassigned
	77 (sh), 65m, 59m, 53 (sh), 46 (sh)	66ms, 52s	$[CuI_3]^{2-}$ bending
$[PMePh_3]_2[AgI_3]$	133s		ν(Ag–I) E'
		105m, 79m	unassigned
	71m, 59s, 47w		$[AgI_3]^{2-}$ bending
$[PMePh_3]_2[CuBr_3]$	190s		ν(Cu–Br) E'
	98m, 64m, 50w		$[CuBr_3]^{2-}$ bending
$[PMePh_3]_2[CuBr_2]Br$	310s		ν(Cu–Br) Σu^+
	79vs		δ(Br–Cu–Br) Πu
$[PMePh_3][CuCl_2]$	405ms		ν(Cu–Cl) Σu^+
	111s		δ(Cl–Cu–Cl) Πu
$[PMePh_3]_3[AgBr_4]$	187 (sh), 174 (sh), 160ms, 140ms	195w, 175 (sh)	ν(Ag–Br)
	92 (sh), 79m, 60s		δ(Br–Ag–Br)
$[PMePh_3][CuBr_2]$	218w, 197s, 172m		ν(Cu–Br)
	110w, 100w, 77s, 60m		δ(Br–Cu–Br)

activity of the fundamental modes of vibration are A_1'(Raman) + A_2''(i.r.) + 2 E' (i.r., Raman).[21a] The totally symmetric A_1' mode is a pure M–X bond stretching mode, while the A_2'' mode is pure out-of-plane bending. Of the two E' modes, one involves mainly bond stretching, and is therefore expected to be at higher frequency than the other, which involves mainly in-plane bending.

The far-i.r. spectrum of $[PMePh_3]_2[CuI_3]$ (Figure 4) shows a strong band at *ca.* 160 cm^{-1} and a number of weaker bands around 60 cm^{-1}. All of the bands at higher wavenumbers can be assigned to vibrations of the cation. The band at 160 cm^{-1} is assigned to the E' ν(Cu–I) mode of the anion. Although the anion does not have exact D_{3h} symmetry in the solid, the distortion from the ideal symmetry is apparently insufficient to split the doubly degenerate E' band. A splitting of about 8 cm^{-1} is clearly resolved in this band in $[AsMePh_3]_2[CuI_3]$, however, so the distortion of the anion from D_{3h} is probably greater in this compound. The wavenumber of ν(Cu–I) in $[CuI_3]^{2-}$ is lower than that of the i.r.-active bond stretching modes of $[CuI_2]^-$ (279 cm^{-1}). This is not unexpected, since it is well known that metal–ligand bond stretching frequencies decrease as the co-ordination number of the metal increases.[22]

The E' ν(Cu–I) mode should also be Raman active. Weak bands occur in the 150—180 cm^{-1} region in the Raman spectra of the $[CuI_3]^{2-}$ compounds, but the assignment of these remains indefinite, because of their low intensity. The bands at *ca.* 60 cm^{-1} in the i.r. and Raman spectra could be due to bending modes. Two such modes ($A_2'' + E'$) are expected for a D_{3h} ion, and three if the lower than three-fold site symmetry causes a splitting of the E mode. More than three bands are seen as poorly resolved multiplets in the 50—70 cm^{-1} region in the far-i.r. spectra, and since coincidences in the i.r. and Raman spectra are not exact, no definite assignments can be made. Definite assignments can also not be made for the totally symmetric A_1' ν(Cu–I) mode, which is expected to be Raman active only, since no strong band could be found at even approximately the same wavenumbers in the Raman spectra of $[PMePh_3]_2[CuI_3]$ and $[AsMePh_3]_2[CuI_3]$. Thus the only definite assignment for these compounds is the asymmetric E' ν(Cu–I) mode at *ca.* 160 cm^{-1}.

The far-i.r. spectrum of $[PMePh_3]_2[AgI_3]$ shows a strong ν(Ag–I) band at *ca.* 130 cm^{-1} (Figure 4). The presence of a single ν(Ag–I) band and the similarity of the far-i.r. spectra in general suggest a mononuclear structure for the anion similar to that for the $[CuI_3]^{2-}$ compounds.

Two compounds of stoicheiometry $[PMePh_3]_2[CuBr_3]$ were prepared. The far-i.r. spectra of these are shown in Figure 5. One appears to contain discrete $[CuBr_3]^{2-}$ ions, as it shows a single strong band at about 190 cm^{-1}, which is assigned to the E' ν(Cu–Br) mode of the anion. The other is formulated as $[PMePh_3]_2[CuBr_2]Br$ on the basis of its far-i.r. spectrum, which contains strong bands at 310 and 79 cm^{-1}. These lie at about the same wavenumber as those found previously for compounds containing discrete $D_{\infty h}$ $[CuBr_2]^-$ ions.[12] Further support for this conclusion comes from the n.q.r. spectrum of this compound (see below).

The i.r. active ν(M–X) vibrations in $[MX_3]^{2-}$ lie at lower wavenumbers than those of the corresponding $[MX_2]^-$ ions. This suggests that the bond-stretching force constants for $[MX_3]^{2-}$ are lower than those for $[MX_2]^-$. The general valence force field for $[MX_3]^{2-}$ consists of at least four force constants: f_r (M–X bond stretching), f_{rr} (M–X, M–X bond interaction), f_α (in-plane X–M–X angle bending), and f_θ (out-of-plane angle bending).[21b] The off-diagonal force constants involving angle bending co-ordinates have been neglected here. The frequencies of all four fundamental vibrational modes would be required to determine the above force constants completely. However, if it is assumed that f_α is negligible compared with $f_r - f_{rr}$, the latter force constant difference can be calculated from the E' ν(M–X) frequency, ν_3, by means of equation (1),[21b] where

$$4\pi^2\nu_3^2 = (\mu_X + \tfrac{3}{2}\mu_M)(f_r - f_{rr}) \qquad (1)$$

μ_M and μ_X are the reciprocal masses of the atoms M and X respectively. This approximation is admittedly crude, but allows an estimate of the upper limit of $f_r - f_{rr}$ to be obtained. The separate force constants f_r and f_{rr} can only be obtained if the A_1' frequency ν_1 is known. This allows calculation of the quantity $f_r + 2f_{rr}$ from equation (2).[21b] This cannot be done

$$4\pi^2\nu_1^2 = (f_r + 2f_{rr})\mu_X \qquad (2)$$

for the $[MX_3]^{2-}$ species at present, since the A_1' mode cannot be definitely assigned, so only $f_r - f_{rr}$ has been calculated. The values obtained lie in the range (0.5—0.6) × 10^2 N m^{-1}, and these quantities are compared in Figure 6 with those for the corresponding MX and $[MX_2]^-$ species.[11] Changes in $f_r - f_{rr}$ are expected to be due mainly to changes in f_r (f_{rr} is 10—20% of f_r in the $[MX_2]^-$ complexes [11,12]) so the regular decrease in this quantity from MX to $[MX_3]^{2-}$ seen in Figure 6 is mainly due to the progressive weakening of the M–X bond as the co-ordination number of the metal increases.

The compound $[PMePh_3][CuBr_2]$, unlike the corresponding

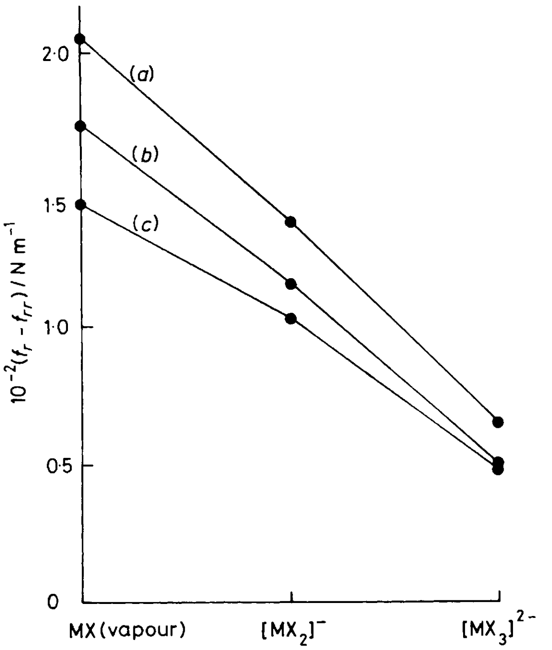

Figure 6. Force constant difference ($f_r - f_{rr}$) for $MX_n^{(1-n)}$ complexes: (*a*) M = Cu, X = Br; (*b*) M = Cu, X = I; and (*c*) M = Ag, X = I

chloro-complex, does not contain discrete mononuclear anions in the solid state. This is evident from the far-i.r. spectrum which shows a number of bands in the 170—220 cm^{-1} region, but none near the value 320 cm^{-1} expected for $[CuBr_2]^-$.[11,12]

The compound $[PMePh_3]_3[AgBr_4]$, which was obtained in attempts to prepare $[PMePh_3]_2[AgBr_3]$, shows at least four incompletely resolved bands in the 140—190 cm^{-1} region in the far-i.r. (Table 3). These are assigned as ν(Ag–Br) modes, but are clearly greater in number than the single T_2 mode expected for an undistorted T_d $[AgBr_4]^{3-}$ ion.

Attempts to prepare compounds $[cation]_2[AgX_3]$ {cation = $[NEt_4]^+$, $[NPr_4]^+$, $[AsPh_4]^+$, $[PPh_4]^+$, and $[N(PPh_3)_2]^+$} by reaction of the appropriate halide with AgX in a 2 : 1 mol ratio resulted either in the formation of compounds of different stoicheiometry {*e.g.*, $[NEt_4][Ag_2Cl_3]$, $[NPr_4]_3[AgBr_4]$, $[AsPh_4]_3[Ag_2Cl_5]$, $[PPh_4][AgBr_2]$, or $[N(PPh_3)_2][AgCl_2]$} or compounds of the desired stoicheiometry (*e.g.*, $[NPr_4]_2[AgI_3]$) whose far-i.r. spectra contain too many bands to be due to mononuclear, planar $[MX_3]^{2-}$ species. The last compound and a number of other compounds $[cation]_2[AgI_3]$ (cation = K^+, $[NH_4]^+$, $[NMe_4]^+$, $[NEt_4]^+$, or $[NBu_4]^+$) have been reported by other workers who claim, on the basis of the Raman spectra of the solids, that those with smaller cations contain C_{3v} pyramidal anions, while those with the larger cations ($[NEt_4]^+$, $[NPr_4]^+$, or $[NBu_4]^+$) contain C_s pyramidal anions.[23] However the structure of $K_2[AgI_3]$ is known,[13] and the anion has an infinite polymeric structure of linked AgI_4 tetrahedra. Also, the compound $Rb_2[AgI_3]$ is isostructural with $K_2[AgI_3]$ and its Raman spectrum (which contains no bands above 112 cm^{-1}) can be satisfactorily analyzed in terms of the infinite polymeric structure.[15] Thus it appears that none of the compounds studied previously contains discrete $[AgI_3]^{2-}$ ions.

N.Q.R. Spectra.—The n.q.r. spectra are listed in Table 4. The nuclei ^{63}Cu (69.1% natural abundance), ^{65}Cu (30.9%), ^{79}Br (50.6%), and ^{81}Br (49.4%) all have nuclear spin $I = \frac{3}{2}$, so only one transition $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ is expected for each of these nuclei.[24a] Signals for both isotopes of copper and bromine were observed with the appropriate frequency ratios, and only the ^{63}Cu and ^{79}Br results are listed in Table 4. Iodine-127 (100% natural abundance) has nuclear spin $I = \frac{5}{2}$, so two transitions, $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ and $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$, are expected in this case.[24a]

Table 4. N.q.r. frequencies at *ca.* 298 K in some trihalogenometalates and related complexes

Compound	N.q.r. frequency/ MHz	Assignment
$[NBu_4][CuBr_2]$ *	28.25	^{63}Cu $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	72.65	^{79}Br $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
$[PMePh_3]_2[CuBr_2]Br$	27.47	^{63}Cu $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	68.90	^{79}Br $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	72.60	^{79}Br $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
$[PMePh_3]_2[CuI_3]$	26.29	^{63}Cu $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	57.34	^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	61.10	^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	96.74	^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$
	103.60	^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$
	108.28	^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$
$[PMePh_3]_2[AgI_3]$	60.36	^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	63.66	^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	64.87	^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$
	111.27	^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$

* Ref. 12.

The complex $[PMePh_3]_2[CuI_3]$ showed a single ^{63}Cu resonance, two ^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ resonances, and three ^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$ resonances. Since the crystal structure of the compound shows that all three iodine atoms are inequivalent, a total of six ^{127}I transitions is expected. The occurrence of only two $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ signals is probably due to accidental coincidence of two of the expected three signals. Indeed the higher frequency member of the pair has approximately twice the intensity of the other, so this is assigned as an accidentally degenerate pair of transitions. The frequencies of the inequivalent iodine atoms do not differ very much, indicating that the electronic environments of each atom are similar to each other.

The complex $[PMePh_3]_2[AgI_3]$ showed three ^{127}I $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ resonances, but only one ^{127}I $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$ resonance. The signals for this compound were significantly weaker than those for the corresponding copper compound, and it is possible that some of the $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$ signals were not detected. The simplest explanation for the presence of three $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ signals within a small frequency range is that this compound, like the corresponding copper compound, contains three crystallographically inequivalent but chemically similar iodine atoms in an isolated $[AgI_3]^{2-}$ species.

The compound formulated as $[PMePh_3]_2[CuBr_2]Br$ on the basis of its vibrational spectrum (see above) gave copper and bromine n.q.r. signals at almost exactly the same frequencies as those in other salts, such as $[NBu_4][CuBr_2]$, which contain discrete $[CuBr_2]^-$ ions (Table 4). This lends further support to the conclusion that this compound contains non-interacting $[CuBr_2]^-$ and Br^- ions. Since a single ^{63}Cu resonance and two ^{79}Br resonances were found in this compound, it appears that the $[CuBr_2]^-$ ion in this complex is distorted from ideal $D_{\infty h}$ symmetry in a way which makes the two Br atoms in the ion symmetrically inequivalent.

The quadrupole resonance frequencies give information about the structure and bonding in the complexes. Firstly, it can be noted that the copper n.q.r. frequencies in $[PMePh_3]_2[CuI_3]$ are similar to those for several other copper(I) complexes containing a copper atom in a trigonal planar environment

Table 5. Nuclear quadrupole coupling parameters

Compound	Nucleus	$\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$/MHz	$\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$/MHz	η	(e^2qQ/h)/MHz
$[Cu(PPh_3)_2Br]$ *	^{63}Cu	32.36		0.113	64.58
	^{81}Br	55.28		0.519	105.91
$[PMePh_3]_2[CuI_3]$	^{63}Cu	26.29		0	52.58
	^{127}I	57.34	96.74	0.39	331.7
		61.10	103.60	0.38	355.0
		61.10	108.28	0.32	368.8

* Ref. 31.

with three equivalent ligands: $[Cu(SPMe_3)_3][ClO_4]$,[25,26] $[PMePh_3]_2[Cu_4I_6]$,[4,5] and $[\{Cu(S_2CNR_2)\}_4]$ (R = Et, Bu, or Pr).[27] The ^{63}Cu frequencies for these compounds all lie in the range 25—27 MHz. The metal–ligand bonds in these complexes are apparently very similar. The mechanism of the copper quadrupole coupling in digonally and trigonally co-ordinated copper(I) complexes has been discussed previously, and it was found that the coupling constants are larger than those expected on the basis of *sp* or *sp*^{2} hybridization schemes.[12,28] Similar results have been obtained for ^{197}Au coupling constants in digonally co-ordinated gold(I) complexes.[28] However, it has been more recently shown that the sign of the coupling constant in $K[Au(CN)_2]$ is opposite to that expected on the basis of the alternative *ds* hybridization scheme.[29] Thus current evidence favours the *sp* hybridization scheme, where the field gradient responsible for the quadrupole coupling is due to electron density in the 4*p* (Cu) or 6*p* (Au) orbitals, due to transfer of electron density from the ligand donor orbital to the vacant *sp* or *sp*^{2} hybrid orbital on the metal.[30] According to this explanation, the ligands involved in the complexes discussed above must all have similar donor strengths with respect to the copper(I) atom.

From the $\nu(\frac{1}{2} \longleftrightarrow \frac{3}{2})$ and $\nu(\frac{3}{2} \longleftrightarrow \frac{5}{2})$ frequencies for a single iodine atom, the quadrupole coupling constant e^2qQ and field gradient asymmetry parameter η can be calculated. The crystallographic inequivalence of the three iodine atoms in $[PMePh_3]_2[CuI_3]$ causes some uncertainty in the assignment of pairs of frequencies to single iodine atoms. However, since the crystal structure shows that the departure from D_{3h} symmetry is small, it seems reasonable to assign the frequencies as shown in Table 5. This produces the smallest spread of values for the quadrupole coupling parameters for the three iodine atoms. Alternative assignments would increase the spread of values, but would not alter the average values very much. The ^{127}I quadrupole coupling parameters calculated from these frequencies are listed in Table 5. Also listed in this Table are the ^{81}Br parameters, which have been recently published for the trigonal planar complex $[Cu(PPh_3)_2Br]$.[31]

The parameter η depends on the degree of departure of the electronic charge distribution about the nucleus in question from axial symmetry. For three-fold or higher symmetry, $\eta = 0$, while for two-fold or lower symmetry, $0 < \eta < 1$. The local symmetry of the iodine atoms in the D_{3h} $[CuI_3]^{2-}$ ion is C_{2v}, so an asymmetry parameter greater than zero is expected. The magnitude of η depends on the relative populations of the I 5*p* ' π ' orbitals (*i.e.* the *p* orbitals perpendicular to the Cu–I bond direction). If these populations differ, for example, as a result of out-of-plane π bonding involving donation of charge from the doubly occupied iodine 5*p* orbital to the vacant copper 4p_x orbital (the *x* direction is defined as perpendicular to the plane of the ion), then a non-zero asymmetry parameter would result. Equation (3) relates the π bond order, π, to the measured values of e^2qQ and η

$$\pi = \tfrac{2}{3}(e^2qQ/e^2q_{at}Q)\eta \qquad (3)$$

($e^2q_{at}Q$ is the coupling constant for the free atom).[24b] This equation has been applied previously to many halogen-containing organic molecules, and to some inorganic and co-ordination compounds such as BBr_3, BI_3, and $[Cu(PPh_3)_2Br]$.[31] The results of the application of this equation to the latter compounds are compared with those for $[CuI_3]^{2-}$ in Table 6. It is evident that π is small in the copper complexes, suggesting that metal–ligand π bonding is not very important in these compounds. However, it is necessary to point out that in the derivation of equation (3) it is assumed that only the out-of-plane π orbital is involved in the π bonding. In-plane π bonding is however symmetry allowed in compounds such as those listed in Table 6, and if this were to take place to the same extent as the out-of-plane bonding, then the populations of the two π orbitals would be the same, and η would be zero, despite the presence of π bonding. In fact, equation (3) measures only the difference between the out-of-plane and in-plane π bond orders π_x and π_y. Thus $\pi = \pi_x - \pi_y$, and the absolute π bond orders remain unknown. This point does not seem to have been appreciated in some previous applications of equation (3).

Table 6. π Bonding parameters for the halogen atoms in $[CuI_3]^{2-}$ and some related compounds

Compound	π
$[Cu(PPh_3)_2Br]$ *	0.06
$[CuI_3]^{2-}$	0.04
BBr_3 *	0.13
BI_3 *	0.16

* Ref. 31.

The ^{127}I coupling constant depends on the degree of ionic character, *i*, of the metal–iodine bond, as well as on the π bonding parameters. The appropriate equation (assuming no *sp* hybridization at iodine) is equation (4).[24c] The free-atom

$$e^2qQ = [1 - i - \tfrac{1}{2}(\pi_x + \pi_y)]e^2q_{at}Q \qquad (4)$$

coupling constant $e^2q_{at}Q/h$ = 2 292.7 MHz for ^{127}I.[24d] The ratio $e^2qQ/e^2q_{at}Q$ lies in the range 0.15—0.16 for the three inequivalent I atoms in $[PMePh_3]_2[CuI_3]$. This can be compared with the values 0.18 and 0.20 for $[CuCl_2]^-$ and $[CuBr_2]^-$ respectively.[12] The similarity of these values indicates a similarity in the type of bonding involved. If it is assumed that π bonding is negligible, then these values imply ionic characters of 0.82, 0.80, and 0.85 in $[CuCl_2]^-$, $[CuBr_2]^-$, and $[CuI_3]^{2-}$ respectively. It has been shown that for equal donation of charge from each ligand to the metal, the metal atom coupling constant for an *sp*^{2} ML_3 (M = d^{10} metal) system is equal to that of the corresponding *sp* ML_2 system.[32] The present results show that I^- donates significantly less charge in $[CuI_3]^{2-}$ than does Cl^- in $[CuCl_2]^-$, so that a lower copper coupling constant for $[CuI_3]^{2-}$ is expected, as observed. Thus a consistent interpretation of the halogen and copper n.q.r. frequencies for these compounds is possible.

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