Structural and Far-infrared Studies of Compounds containing the Novel Trinuclear Iodocuprate(I) Complex $[Cu_3(AsPh_3)_3I_4]^-$ †

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Single-crystal *X*-ray diffraction and far-i.r. spectroscopy have been used to characterize a new type of ionic copper(I) complex. The anion in two crystalline forms (α and β) of $[AsPh_3Me][Cu_3(AsPh_3)_3I_4]$ contains three $AsPh_3$ ligands co-ordinated to the copper atoms of a Cu_3I_4 unit. This unit consists of an apical iodine atom which is bound in a triply bridging bonding mode to three equivalent copper atoms. Adjacent pairs of copper atoms are further connected by doubly bridging iodine atoms. The co-ordination environment of each copper atom is pseudo-tetrahedral, the fourth co-ordination site being occupied by a terminally bonded $AsPh_3$ ligand. The average bond lengths in the anion are Cu–I_t 2.73(1) (I_t = triply bridging iodine), Cu–I_d 2.63(2) (I_d = doubly bridging iodine), and Cu–As 2.38(1) Å. The α-form is monoclinic, space group $P2_1/n$, a = 18.098(5), b = 32.76(2), c = 26.95(2) Å, β = 110.21(3)°, Z = 8, R = 0.072 for 10 331 'observed' [$I > 3\sigma(I)$] reflections. The β-form is monoclinic, space group $P2_1/c$, a = 17.685(4), b = 12.028(5), c = 35.156(6) Å, β = 94.29(2)°, Z = 4, R = 0.051 for 5 584 'observed' [$I > 3\sigma(I)$] reflections. The two forms are solvated by 1.5 CH_2Cl_2 and 1 $CHCl_3$ respectively. The structure of the anion is closely related to that of the neutral tetranuclear 'cubane' complex $[Cu_4(AsPh_3)_4I_4]$, from which it is derived by removal of a $[Cu(AsPh_3)]^+$ unit. The far-i.r. spectrum of $[AsPh_3Me][Cu_3(AsPh_3)_3I_4]$ shows a band at 138 cm^{-1} which is assigned to the Cu–I stretching modes of the Cu_3I_4 unit. Attempts to prepare complexes of the same stoicheiometry with PPh_3 in the place of $AsPh_3$ were unsuccessful. However, changing the cation from $[AsPh_3Me]^+$ to $[PPh_3Me]^+$ resulted in the formation of the compound $[PPh_3Me][Cu_3(AsPh_3)_3I_4]$ which gave a far-i.r. spectrum similar to that of the corresponding $[AsPh_3Me]^+$ compound with a Cu–I stretching frequency of 134 cm^{-1}.

Copper(I) exhibits a remarkable diversity in its structural chemistry, as is demonstrated by the wide variety of structural types encountered in its halide complexes. Copper(I) halides form mono- or multi-nuclear complexes with neutral phosphine or amine ligands in which the copper co-ordination number ranges from two to four.[1–3] 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; in such complexes the co-ordination number four is only found in oligomeric or infinite polymeric structures.[1,2,4–7]

Little 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.* $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_4X_6]^{2-}$, *etc.*) with neutral ligands such as phosphines and amines. We have recently shown[8] that the anionic bromocuprate(I) complex $[CuBr_2]^-$ reacts with 1 mol of triphenylphosphine to yield the species $[Cu(PPh_3)Br_2]^-$, in which the copper(I) ion has the unusual co-ordination number of three. 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] In contrast to the cases of $[CuBr_2]^-$ and $[CuI_2]^-$, $[CuCl_2]^-$ appears not to form any complex with PPh_3.[9] However, $[CuCl_2]^-$ does form a complex, $[Cu(dpa)Cl_2]^-$, with the bidentate ligand di(2-pyridyl)amine (dpa) yielding a pseudo-tetrahedral co-ordination environment about the copper atom.[10] Thus, the type of complex formed in this kind of reaction appears to be strongly dependent upon the nature of the ligand as well as on the particular halide (chloride, bromide, or iodide) involved.

The aim of the present study was to examine further the effect of changing the nature of the ligand in such reactions. The ligand triphenylarsine was chosen because of its close structural and chemical similarity to PPh_3. The only well characterized species which we have been able to prepare to date from the interaction of this ligand with iodocuprate(I) species is the novel trinuclear complex $[Cu_3(AsPh_3)_3I_4]^-$. We report here the preparation of several compounds containing this anion, and their characterization by *X*-ray diffraction and far-i.r. spectroscopic studies.

Experimental

Preparation of Compounds.—Methyltriphenylarsonium tetraiodotricuprate(I), $[AsPh_3Me][Cu_3I_4]$. This was prepared by a previously described method.[7]

Methyltriphenylarsonium tetraiodotris(*triphenylarsine*)*tri-*

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

cuprate(I), [AsPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$]. The salt [AsPh$_3$Me][Cu$_3$I$_4$] (0.51 g, 0.5 mmol) and triphenylarsine (0.46 g, 1.5 mmol) were added to dichloromethane (10 cm^3) and the mixture stirred until all the solid material had dissolved. The colourless product precipitated from the resulting solution within 15 min. M.p. 195—196 °C (Found: C, 44.3; H, 3.4; Cu, 9.9; I, 26.3. Calc. for $C_{73}H_{63}As_4Cu_3I_4$: C, 45.2; H, 3.3; Cu, 9.8; I, 26.2%). An identical product was obtained by using copper(I) iodide (0.29 g, 1.5 mmol) and methyltriphenylarsonium iodide (0.22 g, 0.5 mmol) in place of [AsPh$_3$Me][Cu$_3$I$_4$] in the above preparation. The crystals for the *X*-ray diffraction study were obtained by recrystallization from dichloromethane–diethyl ether (α form) or from chloroform (β form).

Methyltriphenylphosphonium tetraiodotris(triphenylarsine)tricuprate(I), [PPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$]. Copper(I) iodide (0.29 g, 1.5 mmol), methyltriphenylphosphonium iodide (0.20 g, 0.5 mmol), and triphenylarsine (0.46 g, 1.5 mmol) were added to dichloromethane (10 cm^3) and the mixture stirred until all the solid material had dissolved. The colourless product (0.85 g, 89%) precipitated from the resulting solution within 15 min. M.p. 198—199 °C (Found: C, 46.2; H, 3.3. Calc. for $C_{73}H_{63}As_3Cu_3I_4P$: C, 46.3; H, 3.4%).

Structure Determinations.—The initial preparation and crystallization of [AsPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$] from CH$_2$Cl$_2$–Et$_2$O yielded well formed crystals which comprised the subject of the first determination (α form); a later synthesis with recrystallization from CHCl$_3$ yielded a new phase (β form) which was also the subject of a determination with the expectation that, with a material of this complexity, a significantly different stoicheiometry, stereochemistry, or conformation might result. In the event this was not realized, the two materials simply being different solvates of the same compound, losing solvent at about 100 °C and melting at 195 °C.

Unique data sets were measured at $\approx$295 K on specimens mounted in capillaries using an Enraf-Nonius CAD-4 'four-circle' diffractometer [conventional 2θ—θ scan mode; monochromatic Mo-K_α radiation (λ = 0.710 69 Å)]. *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the block-diagonal least-squares refinement after absorption correction and solution of the structures by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms [exception: C(211)(anion 1) in the α form]. For both structures $(x, y, z, U_{iso})_H$ were included constrained at estimated values. The thermal amplitudes were large at the peripheries of the ligands; for both forms, although accessible data were limited, solvent molecules were located and refined sensibly with unit site occupancy, albeit with high thermal motion. Residuals on $|F|$ at convergence are conventional R, R'; statistical weights used were derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.000n_w\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed,[11] and computation used the XTAL 2.6 program system.[12] Non-hydrogen atom co-ordinates are given in Table 1. The structures of the anions are shown in Figure 1.

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

Crystal data. α Form, [AsPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$]·1.5CH$_2$Cl$_2$. $C_{73}H_{63}As_4Cu_3I_4 \cdot 1.5CH_2Cl_2$, M = 2 065.6, monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14, variant), a = 18.098(5), b = 32.76(2), c = 26.95(2) Å, β = 110.21(3)°, U = 14 992 Å^3, $D_c(Z = 8)$ = 1.83 g cm^{-3}, $F(000)$ = 7 960, μ_{Mo} = 42 cm^{-1}, specimen 0.50 × 0.55 × 0.25 mm, $A^*_{min.,max.}$ = 2.49, 4.79 (analytical correction), $2\theta_{max.}$ = 50°, N = 26 353, N_o = 10 331, R = 0.072, R' = 0.069 (n_w = 5).

β Form, [AsPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$]·CHCl$_3$. $C_{73}H_{63}As_4Cu_3I_4 \cdot CHCl_3$, M = 2 057.6, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 17.685(4), b = 12.028(5), c = 35.156(6) Å, β = 94.29(2)°, U = 7 457 Å^3, $D_c(Z = 4)$ = 1.86 g cm^{-3}, $F(000)$ = 3 960, μ_{Mo} = 43 cm^{-1}, specimen 0.18 × 0.32 × 0.20 mm, $A^*_{min.,max.}$ = 1.96, 2.11 (Gaussian correction), $2\theta_{max.}$ = 45°, N = 8 795, N_o = 5 584, R = 0.051, R' = 0.053 (n_w = 4).

Far-i.r. Spectra.—Far-i.r. spectra were recorded at room temperature as petroleum jelly mulls between Polythene plates or as pressed Polythene discs on a Digilab FTS-60 Fourier-transform spectrometer employing a FTS-60V vacuum optical bench with a 6.25 μm mylar-film beam splitter, a mercury-lamp source, and a TGS detector, and on a Nicolet 20F Fourier-transform spectrometer.

Results and Discussion

Copper(I) iodide, iodide ion, and triphenylarsine combine in a 3:1:3 ratio to form tetraiodotris(triphenylarsine)tricuprate(I) ion, [Cu$_3$(AsPh$_3$)$_3$I$_4$]$^-$, which was crystallized from dichloromethane as its [AsPh$_3$Me]$^+$ and [PPh$_3$Me]$^+$ salts. Attempts to prepare the corresponding PPh$_3$ complex, [Cu$_3$(PPh$_3$)$_3$I$_4$]$^-$, by carrying out the same reactions with PPh$_3$ in place of AsPh$_3$ were unsuccessful, mixtures of several products being obtained.

X-Ray Structure Determinations.—The structures of the [Cu$_3$(AsPh$_3$)$_3$I$_4$]$^-$ ion in the two different solvates of [AsPh$_3$Me][Cu$_3$(AsPh$_3$)$_3$I$_4$] are shown in Figure 1; in the α form, there are two crystallographically independent species. In this ion three AsPh$_3$ ligands are co-ordinated to the copper atoms of a Cu$_3$I$_4$ unit. The Cu$_3$I$_4$ unit consists of an apical iodine atom which is bound in a triply bridging bonding mode to three equivalent copper atoms. Adjacent pairs of copper atoms are further connected by doubly bridging iodine atoms. The co-ordination environment of each copper atom is pseudo-tetrahedral, the fourth co-ordination site being occupied by a terminally bonded AsPh$_3$ ligand. None of the species has any crystallographically imposed symmetry. Selected bond lengths and bond angles for the As$_3$Cu$_3$I$_4$ core are given in Table 2. Some average bond lengths in the anion are Cu–I$_t$ 2.73(1) (I$_t$ = triply bridging iodine), Cu–I$_d$ 2.63(2) (I$_d$ = doubly bridging iodine), and Cu–As 2.38(1) Å. The structure of the anion is closely related to that of the neutral tetranuclear complex [Cu$_4$(AsPh$_3$)$_4$I$_4$], which has a 'cubane' structure.[13] Removal of a [Cu(AsPh$_3$)]$^+$ unit from this structure results in a [Cu$_3$(AsPh$_3$)$_3$I$_4$]$^-$ species with a structure essentially the same as that found in the present work. The core geometry of the [Cu$_3$(AsPh$_3$)$_3$I$_4$]$^-$ complex is compared in Table 3 with those of the species [Cu$_4$(AsPh$_3$)$_4$I$_4$] and [Cu$_4$(PPh$_3$)$_4$I$_4$] ('cubane' forms).[13,14] Most of the corresponding parameters for the two AsPh$_3$ complexes are similar in magnitude. Although there is a significant difference between the average Cu–I bond lengths for the triply and doubly bridging iodides in [Cu$_3$(AsPh$_3$)$_3$I$_4$]$^-$ (see above), the range of Cu–I bond lengths in this complex is not very much greater than that for [Cu$_4$(AsPh$_3$)$_4$I$_4$]. The As–Cu–I and I–Cu–I bond angles are all fairly evenly distributed about the tetrahedral angle (109.5°), indicating that there are only slight distortions from tetrahedral geometry about the copper atoms. The Cu–I–Cu angles are quite acute, and the ranges of values for the two AsPh$_3$ complexes are very similar, and are significantly smaller than those for [Cu$_4$(PPh$_3$)$_4$I$_4$]. This is also reflected in the significantly shorter Cu $\cdots$ Cu distances in the AsPh$_3$ complexes. The tri- and tetranuclear complexes in Table 3 can be considered to be made up of three or four LCuI$_3$ tetrahedra which are linked by sharing the edges of the I$_3$ faces of the tetrahedra. For perfectly regular tetrahedral geometry about the copper atom, it can be shown

Table 1. Non-hydrogen atom co-ordinates

	α1			α2			β		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Anion									
I(1)	0.150 55(7)	0.875 98(5)	−0.003 57(6)	0.396 51(7)	0.371 06(5)	0.062 74(6)	0.190 06(6)	0.264 25(8)	0.338 40(3)
I(12)	0.266 05(8)	0.946 03(5)	−0.097 62(6)	0.281 19(9)	0.440 70(5)	0.157 87(7)	0.088 64(6)	0.564 14(9)	0.383 60(3)
I(13)	0.406 93(7)	0.874 05(6)	0.033 61(6)	0.280 42(9)	0.311 15(5)	0.164 91(7)	0.192 35(7)	0.319 1(1)	0.461 33(3)
I(23)	0.259 96(8)	0.813 31(5)	−0.107 93(6)	0.143 24(7)	0.374 09(5)	0.012 78(6)	0.337 24(6)	0.527 37(9)	0.390 66(3)
Cu(1)	0.279 9(1)	0.919 08(8)	−0.002 6(1)	0.363 0(1)	0.375 0(1)	0.154 6(1)	0.115 7(1)	0.354 9(2)	0.395 58(5)
As(1)	0.278 5(1)	0.978 00(7)	0.049 14(9)	0.488 2(1)	0.376 41(8)	0.223 54(8)	0.002 43(9)	0.252 6(1)	0.401 15(4)
C(111)	0.354(1)	1.019 7(7)	0.050 8(7)	0.568(1)	0.337 9(6)	0.218 2(8)	0.002 7(8)	0.099(1)	0.387 0(4)
C(112)	0.345(1)	1.059 9(6)	0.062 8(9)	0.543(1)	0.305 4(7)	0.187(1)	0.068 8(9)	0.039(1)	0.395 9(4)
C(113)	0.403(2)	1.089 9(8)	0.064(1)	0.601(2)	0.276 8(9)	0.184(1)	0.073 6(9)	−0.073(1)	0.385 4(5)
C(114)	0.469(1)	1.078 1(7)	0.054(1)	0.679(1)	0.286 4(8)	0.209(1)	0.012 1(9)	−0.125(1)	0.366 7(5)
C(115)	0.483(1)	1.037 7(8)	0.047 9(9)	0.702(1)	0.318 5(8)	0.241(1)	−0.050 7(8)	−0.064(1)	0.357 4(4)
C(116)	0.424(1)	1.007 0(7)	0.043(1)	0.649(1)	0.343 8(6)	0.244 7(9)	−0.055 8(8)	0.046(1)	0.367 1(4)
C(121)	0.182(1)	1.010 0(6)	0.025 9(9)	0.484(1)	0.366 7(7)	0.294 6(9)	−0.029 3(8)	0.245(1)	0.452 1(4)
C(122)	0.141(1)	1.021 0(8)	0.057(1)	0.414(1)	0.373 6(7)	0.300 6(7)	−0.044 5(9)	0.146(1)	0.471 2(4)
C(123)	0.075(1)	1.044 8(9)	0.038(1)	0.407(1)	0.369 6(8)	0.349(1)	−0.072 0(9)	0.149(1)	0.506 4(5)
C(124)	0.049(1)	1.058 9(7)	−0.014(1)	0.471(1)	0.354 8(7)	0.392 7(9)	−0.083(1)	0.247(2)	0.523 4(5)
C(125)	0.089(1)	1.049 2(8)	−0.046(1)	0.540(1)	0.347 8(7)	0.386(1)	−0.067 1(9)	0.344(1)	0.506 3(5)
C(126)	0.158(2)	1.022 9(8)	−0.026(1)	0.551(1)	0.352 6(7)	0.338(1)	−0.039 0(9)	0.344(1)	0.471 2(4)
C(131)	0.297(1)	0.972 3(6)	0.123 8(8)	0.546(1)	0.424 9(7)	0.232 6(9)	−0.093 2(8)	0.300(1)	0.374 6(4)
C(132)	0.246(1)	0.948 4(6)	0.141 1(8)	0.583(1)	0.444 5(8)	0.282(1)	−0.163 3(8)	0.285(1)	0.390 3(5)
C(133)	0.261(1)	0.941 8(8)	0.194(1)	0.624(1)	0.482 1(7)	0.288(1)	−0.228 3(9)	0.313(1)	0.367 4(6)
C(134)	0.327(1)	0.957 4(7)	0.231(1)	0.628(1)	0.500 5(8)	0.244(1)	−0.225(1)	0.361(1)	0.333 8(5)
C(135)	0.379(1)	0.978 6(8)	0.215 9(9)	0.594(1)	0.482 7(8)	0.193(1)	−0.156(1)	0.379(1)	0.318 8(5)
C(136)	0.366(1)	0.988 5(6)	0.162 9(9)	0.550(1)	0.445 1(7)	0.189(1)	−0.091 6(9)	0.348(1)	0.340 1(5)
Cu(2)	0.184 7(1)	0.879 44(9)	−0.094 4(1)	0.272 8(2)	0.417 47(9)	0.063 4(1)	0.208 4(1)	0.486 9(2)	0.351 48(5)
As(2)	0.061 3(1)	0.880 64(7)	−0.166 04(9)	0.271 1(1)	0.478 46(7)	0.014 32(9)	0.202 30(9)	0.574 3(1)	0.290 88((4)
C(211)	0.070(1)	0.866 7(6)	−0.233 2(8)	0.249(1)	0.472 5(7)	−0.060 0(9)	0.262 6(8)	0.522(1)	0.252 4(4)
C(212)	0.140(1)	0.877 6(8)	−0.240 3(8)	0.213(2)	0.499(1)	−0.097(1)	0.245 5(9)	0.532(1)	0.214 3(4)
C(213)	0.145(2)	0.871 3(9)	−0.290(1)	0.202(2)	0.492 5(8)	−0.149(1)	0.294(1)	0.496(2)	0.188 0(5)
C(214)	0.082(1)	0.852 1(9)	−0.332(1)	0.224(2)	0.460(1)	−0.166(1)	0.361(1)	0.448(1)	0.199 4(5)
C(215)	0.017(1)	0.841 4(7)	−0.321 6(9)	0.257(2)	0.429(1)	−0.130(1)	0.380(1)	0.436(2)	0.237 8(5)
C(216)	0.010(1)	0.849 1(6)	−0.274 2(9)	0.271(2)	0.438 9(9)	−0.078(1)	0.330 6(9)	0.470(1)	0.263 9(4)
C(221)	−0.023(1)	0.845 0(6)	−0.165 2(8)	0.196(1)	0.518 8(7)	0.016(1)	0.104 2(8)	0.574(1)	0.262 2(4)
C(222)	−0.004(1)	0.804 3(7)	−0.148(1)	0.132(1)	0.506 4(9)	0.030(1)	0.065 2(9)	0.474(1)	0.261 1(5)
C(223)	−0.066(2)	0.779 4(8)	−0.152(1)	0.077(1)	0.536 6(8)	0.032(1)	−0.004 4(9)	0.464(1)	0.239 8(5)
C(224)	−0.141(1)	0.792 5(9)	−0.164(1)	0.083(1)	0.576 0(9)	0.023(1)	−0.035 0(8)	0.555(1)	0.221 3(4)
C(225)	−0.159(1)	0.830 2(9)	−0.179(1)	0.148(2)	0.589 0(9)	0.009(1)	0.001 6(8)	0.654(1)	0.223 4(4)
C(226)	−0.101(1)	0.856 2(8)	−0.182(1)	0.203(1)	0.557 3(8)	0.008(1)	0.073 0(8)	0.664(1)	0.243 8(4)
C(231)	0.004(1)	0.932 0(6)	−0.184 8(8)	0.363(1)	0.511 9(7)	0.033 4(9)	0.227 5(8)	0.733(1)	0.290 4(4)
C(232)	−0.035(1)	0.943 8(6)	−0.236 1(8)	0.400(1)	0.521 7(9)	0.086(1)	0.276(1)	0.777(1)	0.266 1(5)
C(233)	−0.076(1)	0.980 4(8)	−0.248(1)	0.466(2)	0.548 7(8)	0.101(1)	0.294(1)	0.891(2)	0.267 3(6)
C(234)	−0.077(1)	1.005 4(7)	−0.208(1)	0.498(1)	0.558 3(8)	0.063(1)	0.264(1)	0.955(1)	0.293 3(5)
C(235)	−0.037(1)	0.994 7(8)	−0.156(1)	0.467(2)	0.548 9(9)	0.012(1)	0.217 5(9)	0.912(1)	0.317 0(4)
C(236)	0.005(1)	0.961 5(8)	−0.144(1)	0.400(1)	0.525 2(8)	−0.003(1)	0.199 0(9)	0.799(1)	0.315 7(4)
Cu(3)	0.275 7(1)	0.832 20(8)	−0.009 6(1)	0.266 6(2)	0.329 57(9)	0.067 3(1)	0.273 2(1)	0.334 7(2)	0.402 62(5)
As(3)	0.272 8(1)	0.769 97(7)	0.035 79(9)	0.263 9(1)	0.266 21(7)	0.022 57(9)	0.372 60(9)	0.204 1(1)	0.414 10(4)
C(311)	0.177(1)	0.737 9(6)	0.011 3(8)	0.360(1)	0.234 3(7)	0.044 4(9)	0.436 6(8)	0.230(1)	0.461 4(4)
C(312)	0.138(1)	0.720 1(7)	0.042 8(8)	0.394(1)	0.218 6(7)	0.012(1)	0.485 9(8)	0.147(1)	0.475 9(4)
C(313)	0.071(1)	0.696 7(7)	0.020(1)	0.463(1)	0.195 9(9)	0.033(1)	0.531 4(9)	0.170(1)	0.509 3(5)
C(314)	0.044(1)	0.690 5(7)	−0.032(1)	0.497(1)	0.187 1(7)	0.085(1)	0.526 6(9)	0.272(1)	0.526 8(4)
C(315)	0.079(1)	0.705 6(8)	−0.064(1)	0.462(1)	0.200 1(8)	0.120(1)	0.477 3(9)	0.351(1)	0.512 5(4)
C(316)	0.150(1)	0.730 5(8)	−0.040(1)	0.391(1)	0.223 5(9)	0.100(1)	0.431 4(8)	0.329(1)	0.480 1(4)
C(321)	0.290(1)	0.770 9(6)	0.111 7(8)	0.188 7(9)	0.224 4(7)	0.024 8(8)	0.343 7(8)	0.052(1)	0.419 5(4)
C(322)	0.238(1)	0.792 3(6)	0.128 8(9)	0.113(1)	0.240 5(8)	0.020 4(9)	0.362 4(9)	−0.031(1)	0.397 0(4)
C(323)	0.250(1)	0.794 3(8)	0.182(1)	0.059(1)	0.209 0(7)	0.0225(9)	0.336(1)	−0.140(1)	0.398 8(5)
C(324)	0.313(1)	0.774 2(7)	0.219 2(9)	0.076(1)	0.167 3(8)	0.030(1)	0.288 4(8)	−0.163(1)	0.424 9(5)
C(325)	0.365(1)	0.753 3(8)	0.200(1)	0.150(1)	0.155 9(6)	0.034 8(9)	0.267 4(9)	−0.082(1)	0.450 2(5)
C(326)	0.352(1)	0.752 7(7)	0.145 6(9)	0.206(1)	0.182 7(7)	0.031 (1)	0.296 0(9)	0.028(1)	0.447 0(5)
C(331)	0.348(1)	0.728 4(6)	0.032 2(9)	0.244(1)	0.268 3(7)	−0.053(1)	0.445 5(8)	0.199(1)	0.377 6(5)
C(332)	0.338(1)	0.689 0(7)	0.040 1(9)	0.263(2)	0.300 6(9)	−0.071(1)	0.418(1)	0.220(2)	0.341 1(6)
C(333)	0.391(1)	0.659 2(7)	0.037 0(9)	0.247(2)	0.307 5(9)	−0.128(1)	0.465(1)	0.215(3)	0.310 6(7)
C(334)	0.455(2)	0.671 5(9)	0.025(1)	0.222(2)	0.274 5(9)	−0.159(1)	0.542(1)	0.198(2)	0.318 7(7)
C(335)	0.466(1)	0.711 7(9)	0.016(1)	0.203(2)	0.242 1(8)	−0.140(1)	0.568(1)	0.171(2)	0.353 3(6)
C(336)	0.412(2)	0.739 6(8)	0.021(1)	0.213(2)	0.238 2(7)	−0.088(1)	0.519(1)	0.175(2)	0.381 6(5)

Table 1 (*continued*)

	α1			α2			β		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cation									
As	0.499 6(1)	0.871 89(8)	0.226 44(9)	0.005 8(2)	0.615 4(1)	0.199 2(1)	0.203 89(9)	0.334 9(1)	0.585 72(5)
C(11)	0.568(1)	0.909 3(6)	0.209 3(9)	−0.050(1)	0.613 7(7)	0.247 1(9)	0.248 6(8)	0.197(1)	0.572 5(4)
C(12)	0.541(1)	0.935 9(8)	0.170(1)	−0.052(1)	0.578 7(7)	0.277(1)	0.318 8(9)	0.194(1)	0.556 7(5)
C(13)	0.592(1)	0.963 0(8)	0.158(1)	−0.097(2)	0.580 4(8)	0.307(1)	0.347(1)	0.093(2)	0.549 9(6)
C(14)	0.668(1)	0.962 6(7)	0.187(1)	−0.139(1)	0.611 4(9)	0.311(1)	0.310(1)	−0.003(2)	0.555 7(5)
C(15)	0.698(1)	0.935 5(7)	0.230(1)	−0.138(1)	0.646 4(9)	0.285(1)	0.240(1)	0.001(1)	0.568 6(6)
C(16)	0.646(1)	0.910 6(8)	0.241 7(9)	−0.095(1)	0.649 0(7)	0.251(1)	0.208(1)	0.101(1)	0.577 6(6)
C(21)	0.484(1)	0.889 3(7)	0.291 6(9)	0.022(1)	0.672 1(7)	0.186(1)	0.190 0(8)	0.328(1)	0.638 8(4)
C(22)	0.427(1)	0.868 0(8)	0.304 6(8)	−0.016(2)	0.690(1)	0.137(1)	0.123 2(8)	0.356(1)	0.652 9(5)
C(23)	0.415(1)	0.881 3(8)	0.350(1)	−0.003(2)	0.730 8(9)	0.132(1)	0.111(1)	0.349(1)	0.690 6(5)
C(24)	0.459(1)	0.911 9(8)	0.380 8(9)	0.047(2)	0.751 7(8)	0.174(2)	0.168(1)	0.314(1)	0.715 9(5)
C(25)	0.513(2)	0.929(1)	0.367(1)	0.088(2)	0.734 3(9)	0.219(2)	0.234(1)	0.285(2)	0.703 4(5)
C(26)	0.529(1)	0.919(1)	0.323(1)	0.073(2)	0.694(1)	0.229(2)	0.250 1(9)	0.291(1)	0.664 5(5)
C(31)	0.548(1)	0.818 9(6)	0.234 2(9)	0.103(1)	0.589(1)	0.227(2)	0.268 2(9)	0.452(1)	0.572 4(4)
C(32)	0.551(1)	0.801 0(8)	0.190(1)	0.139(2)	0.566(1)	0.201(2)	0.334(1)	0.473(1)	0.595 9(5)
C(33)	0.587(1)	0.762 4(8)	0.195(1)	0.214(3)	0.551(1)	0.227(2)	0.383(1)	0.559(2)	0.582 4(6)
C(34)	0.619(2)	0.743 7(8)	0.241(1)	0.251(2)	0.559(1)	0.279(2)	0.364(1)	0.617(1)	0.551 8(6)
C(35)	0.615(1)	0.763 2(9)	0.284(1)	0.223(2)	0.579(1)	0.315(2)	0.301(1)	0.598(2)	0.530 7(5)
C(36)	0.578(1)	0.802 2(7)	0.284(1)	0.143(2)	0.595 4(9)	0.284(2)	0.252(1)	0.513(1)	0.541 1(5)
C(41)	0.400(1)	0.869 6(8)	0.170 9(9)	−0.045(2)	0.587(1)	0.133(1)	0.105 4(9)	0.349(2)	0.558 4(5)
Solvent*									
C(1)	0.653(2)	0.885(1)	0.076(1)				0.498(2)	0.658(3)	0.325 8(7)
Cl(11)	0.658 6(7)	0.848 4(4)	0.118 8(5)				0.529 1(4)	0.731 9(7)	0.367 5(2)
Cl(12)	0.744 2(9)	0.898 9(6)	0.078 4(7)				0.544 0(6)	0.559(1)	0.313 1(3)
C(2)	0.287(2)	0.641(2)	0.182(2)				0.456 3(8)	0.742(1)	0.296 9(4)
Cl(21)	0.303 8(8)	0.605 4(5)	0.140 7(5)						
Cl(22)	0.200 9(9)	0.662 0(5)	0.163 0(7)						
C(3)	0.676(3)	0.355(1)	0.107(2)						
Cl(31)	0.673(1)	0.402 9(5)	0.121 1(7)						
Cl(32)	0.775(1)	0.355 2(7)	0.103 9(6)						

* For the β form, for Cl(11,12), C(2) read Cl(1,2,3).

that the bridging Cu–I–Cu angles would be 65.96° and that the Cu ··· Cu distance would be equal to 1.09 *d*, where *d* is the Cu–I bond length. The Cu–I–Cu angles in the $AsPh_3$ complexes are all slightly lower than the above value whereas those for $[Cu_4(PPh_3)_4I_4]$ are slightly above. For a mean Cu–I bond length of 2.7 Å the mean Cu ··· Cu distance should be 2.9 Å. Again, the values of the $AsPh_3$ complexes are slightly below this value, whereas those for $[Cu_4(PPh_3)_4I_4]$ are slightly above. Similar effects have been observed previously for $[Cu_4(AsEt_3)_4I_4]$ and $[Cu_4(PEt_3)_4I_4]$,[15] as well as for $[Cu_4(AsPh_3)_4I_4]$ and $[Cu_4(PPh_3)_4I_4]$.[13]

Trinuclear copper(I) complexes are much less common than mono-, bi-, or tetra-nuclear complexes,[1] and the complex reported here represents a new structural type. A closely related structure is shown by the complex $[Cu_3(dppm)_2I_3]$ (dppm = $Ph_2PCH_2PPh_2$).[16] This consists of a Cu_3 triangle which is capped by *two* triply bridging iodide ligands, one on each side of the triangle, a doubly bridging iodide which connects two of the copper atoms on one side of the triangle, and two dppm ligands which bridge the other two sides of the triangle. However, no trinuclear halogenocopper(I) complexes have been reported which contain a Cu_3 triangle capped on only one side by a triply bridging halide. The nearest example of this kind of trinuclear structure is found in the complex $[Cu_3(dppm)_3(OH)][BF_4]_2$ which contains a single triply bridging hydroxide ligand.[17]

The structure found in the present work bears a close relationship to that of the infinite chain of $[Cu_3I_4]^-$ in $[PPh_3Me][Cu_3I_4]$.[18] In this structure, a Cu_3 triangle [consisting of the atoms Cu(1), Cu(2), Cu(3)] is capped by a single triply bridging iodine atom [I(1)]; two of the copper atoms [Cu(1), Cu(3)] are also connected by a doubly bridging iodine atom [I(2)] and the remaining pairs of copper atoms [Cu(1), Cu(2) and Cu(2), Cu(3)] are bridged by iodine atoms which are also connected to adjacent copper atoms in the polymeric structure. The fourth co-ordination site at each copper atom is occupied by an iodine atom which is also connected to adjacent copper atoms in the polymeric structure.[18] The structure of the complex $[Cu_3(AsPh_3)_3I_4]^-$ can be derived from the one described above by removal of a $[Cu_3I_4]^-$ unit from the chain and placement of an $AsPh_3$ ligand at the fourth co-ordination site of each copper atom. The nature of the anionic species present in solutions of salts such as $[PPh_3Me][Cu_3I_4]$ is not known at present. If such solutions contain isolated $[Cu_3I_4]^-$ species, the structure of such a species might be similar to that determined in the present work for $[Cu_3(AsPh_3)_3I_4]^-$, with the $AsPh_3$ ligands replaced by solvent molecules.

Far-i.r. Spectra.—The far-i.r. spectra of the two compounds reported are shown in Figure 2. Assignments of the ν(Cu–I) wavenumbers for these and for some related iodocuprate(I) and PPh_3 and $AsPh_3$ complexes of copper(I) iodide are given in Table 4. Only one band for the $[Cu_3(AsPh_3)_3I_4]^-$ complexes can be unambiguously assigned as ν(Cu–I). This is also true for the species $[Cu(PPh_3)_2I_2]^-$ and $[Cu_2(PPh_3)_2I_3]^-$,[9] and it can be

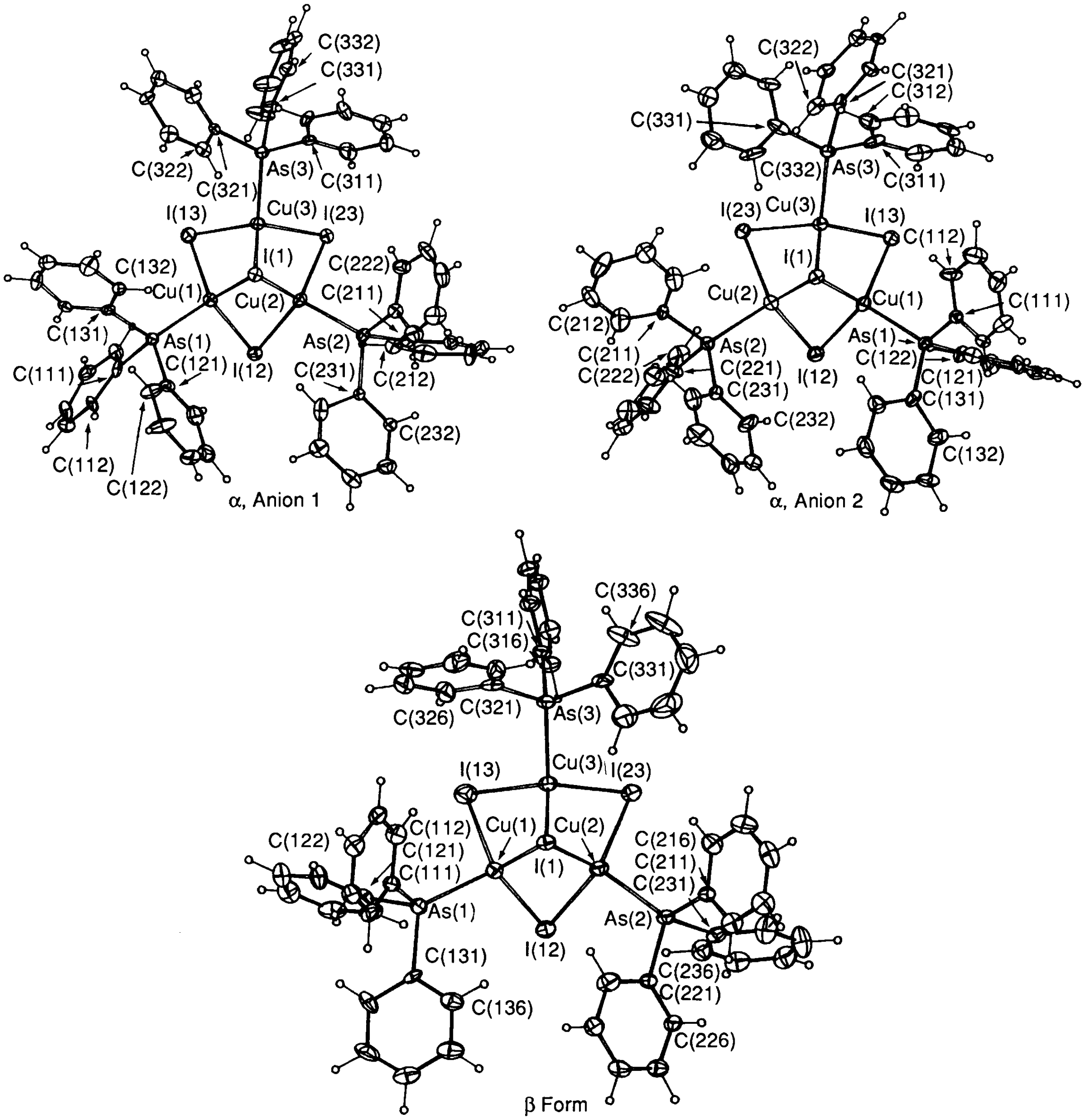

Figure 1. Structure of the three independent anions $[Cu_3(AsPh_3)_3I_4]^-$ projected normal to the I(12, 23, 31) plane. 20% Thermal envelopes are shown for the non-hydrogen atoms, with the labelling scheme. Hydrogen atoms have an arbitrary radius of 0.1 Å

noted that the ν(Cu–I) wavenumber for these latter two complexes shows an increase as the mole ratio r of I^- to CuI in the complex decreases from 1 {in $[Cu(PPh_3)_2I_2]^-$} to 0.5 {in $[Cu_2(PPh_3)_2I_3]^-$}. The complexes $[Cu_4(PPh_3)_4I_4]$ or $[Cu(PPh_3)_3I]$ represent limiting cases in this series ($r = 0$), and their highest-frequency ν(Cu–I) modes occur in the i.r. spectrum at about 140 cm^{-1}. The complex $[Cu_3(AsPh_3)_3I_4]^-$ is an intermediate case ($r = 0.33$), and the average ν(Cu–I) frequency for this complex of about 136 cm^{-1} is consistent with the monotonic relationship between ν(Cu–I) and r noted above.

We have previously found that the metal–halogen vibrational frequencies of the metal–halogen core in phosphinemetal halide complexes can be calculated with reasonable accuracy by carrying out a normal-co-ordinate analysis on the metal–halogen core only.[9,19] In order to check the ν(Cu–I) assignment suggested above, and to investigate further the relationship between the properties of the Cu_3I_4 core in the present complex and the Cu_4I_4 core in the 'cubane' type complexes, we have used this approach to calculate the frequencies of a C_{3v} Cu_3I_4 unit, and to correlate these with the frequencies previously calculated for a T_d Cu_4I_4 unit. A simple diagonal force field was used which involves a Cu–I bond-stretching force constant f_r and an I–Cu–I angle-bending force constant f_α, with $f_\alpha = 0.1f_r$. The geometric and force-constant parameters for the T_d Cu_4I_4 unit were the same as those used in a previous calculation.[19] The correlation between the T_d Cu_4I_4 unit and the C_{3v} Cu_3I_4 unit was made by reducing the force constants for co-ordinates involving the fourth copper atom, Cu(4), to zero. The frequencies of the modes derived from the T_2 and E modes of the T_d Cu_4I_4 unit obtained from these calculations are shown in Figure 3. The frequencies of the modes derived from the A_1 (105, 51 cm^{-1}) and T_1 (130 cm^{-1}) modes of the T_d Cu_4I_4 unit remain almost invariant in the transition to C_{3v} Cu_3I_4, and these have been omitted from Figure 3 for clarity. The results in Figure 3 show that the highest-frequency T_2 mode, which is responsible for the strong i.r. band at about 140 cm^{-1} of the Cu_4I_4 complexes,[19] becomes slightly split, but remains essentially unchanged in frequency in the transition to the Cu_3I_4 unit. This therefore corresponds to the strong i.r. band at about 136 cm^{-1} of the Cu_3I_4 species. The second T_2 mode, which is observed as a strong band at about 100 cm^{-1} for the Cu_4I_4 complexes,[19] is strongly shifted to lower frequency in the Cu_3I_4 case, and is replaced by an E mode, derived from the i.r.-inactive E mode of Cu_4I_4 at about the same frequency. This mode becomes i.r. active in the C_{3v} Cu_3I_4 case, and is possibly responsible for a weak i.r. band observed at about 90 cm^{-1} for the Cu_3I_4 complexes (Figure 2). The Raman spectrum of $[AsPh_3Me][Cu_3(AsPh_3)_3I_4]$ is less well resolved than the far-i.r. spectrum, but band maxima occur at about 110 and 60 cm^{-1}, which are close to the frequencies calculated

Table 2. Anion core geometries (distances in Å, angles in °) in $[AsPh_3Me]$-$[Cu_3(AsPh_3)_3I_4]$

	α1	α2	β
I(1)–Cu(1)	2.727(3)	2.746(4)	2.712(2)
I(1)–Cu(2)	2.726(4)	2.711(3)	2.732(2)
I(1)–Cu(3)	2.734(3)	2.755(3)	2.735(2)
I(12)–Cu(1)	2.637(4)	2.633(4)	2.590(2)
I(12)–Cu(2)	2.650(3)	2.611(4)	2.643(2)
I(13)–Cu(1)	2.619(3)	2.640(4)	2.626(2)
I(13)–Cu(3)	2.639(3)	2.626(4)	2.604(2)
I(23)–Cu(2)	2.651(4)	2.678(3)	2.618(2)
I(23)–Cu(3)	2.638(4)	2.646(3)	2.627(2)
Cu(1)–As(1)	2.386(4)	2.383(3)	2.372(3)
Cu(2)–As(2)	2.394(3)	2.391(4)	2.371(2)
Cu(3)–As(3)	2.388(4)	2.392(4)	2.370(2)
Cu(1) · · · Cu(2)	2.800(4)	2.805(4)	2.827(3)
Cu(2) · · · Cu(3)	2.781(4)	2.885(4)	2.754(3)
Cu(1) · · · Cu(3)	2.852(4)	2.820(4)	2.788(3)
Cu(1)–I(1)–Cu(2)	61.78(9)	61.9(1)	62.56(6)
Cu(1)–I(1)–Cu(3)	62.98(9)	61.68(9)	61.57(6)
Cu(2)–I(1)–Cu(3)	61.23(9)	63.7(1)	60.49(6)
I(1)–Cu(1)–I(12)	111.74(9)	111.7(1)	111.37(8)
I(1)–Cu(1)–I(13)	110.6(1)	111.6(1)	109.85(8)
I(1)–Cu(1)–As(1)	104.0(1)	104.9(1)	108.18(8)
I(1)–Cu(2)–I(12)	111.3(1)	113.6(1)	109.12(7)
I(1)–Cu(2)–I(23)	112.1(1)	106.2(1)	111.02(7)
I(1)–Cu(2)–As(2)	106.7(1)	108.6(1)	106.65(8)
I(1)–Cu(3)–I(13)	109.8(1)	111.7(1)	109.80(7)
I(1)–Cu(3)–I(23)	112.26(9)	105.8(1)	110.67(7)
I(1)–Cu(3)–As(3)	104.6(1)	106.0(1)	106.32(8)
Cu(1)–I(12)–Cu(2)	63.94(9)	64.7(1)	65.38(7)
Cu(1)–I(13)–Cu(3)	65.69(9)	64.8(1)	64.42(7)
Cu(2)–I(23)–Cu(3)	63.44(9)	65.6(1)	63.34(6)
I(12)–Cu(1)–I(13)	109.1(1)	107.4(1)	112.30(8)
I(12)–Cu(1)–As(1)	106.2(1)	110.6(1)	111.73(9)
I(13)–Cu(1)–As(1)	115.0(1)	110.7(1)	103.04(8)
I(12)–Cu(2)–I(23)	110.5(1)	113.4(1)	113.79(8)
I(12)–Cu(2)–As(2)	109.5(1)	106.3(1)	104.11(8)
I(23)–Cu(2)–As(2)	106.5(1)	108.7(1)	111.70(9)
I(13)–Cu(3)–I(23)	109.5(1)	116.9(1)	117.35(8)
I(13)–Cu(3)–As(3)	113.2(1)	106.5(1)	105.15(8)
I(23)–Cu(3)–As(3)	107.5(1)	109.4(1)	106.80(8)

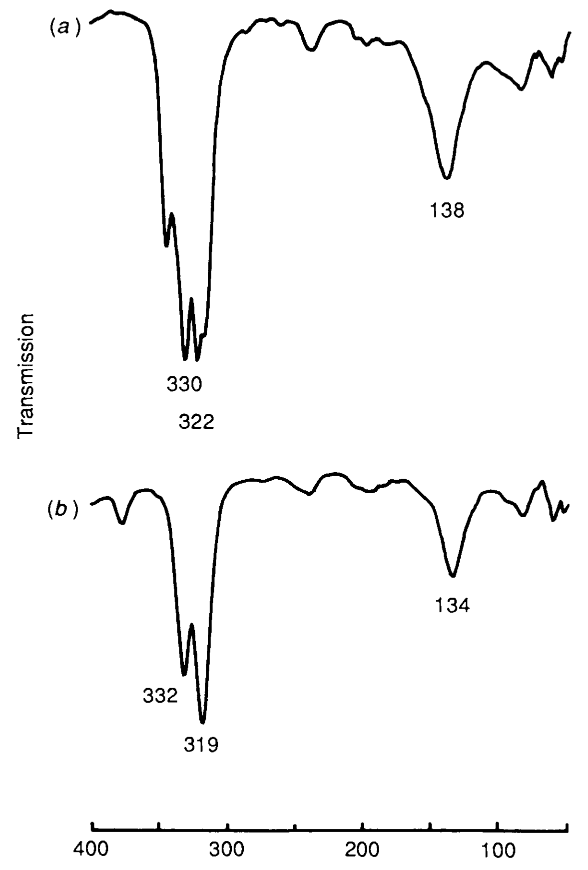

Figure 2. Far-i.r. spectrum of (*a*) $[AsPh_3Me][Cu_3(AsPh_3)_3I_4]$ and (*b*) $[PPh_3Me][Cu_3(AsPh_3)_3I_4]$

Table 4. Highest-wavenumber ν(CuI) bands in the far-i.r. spectra of several iodocopper(I) complexes

Complex	r^s	ν(CuI)/cm^{-1}	Ref.
$[Cu(PPh_3)_2I_2]^-$	1.0	118	9
$[Cu_2(PPh_3)_2I_3]^-$	0.5	127	9
$[Cu_4(PPh_3)_4I_4]$ 'cubane'	0	140	19
$[Cu(PPh_3)_3I]$	0	138	3
$[AsPh_3Me][Cu_3(AsPh_3)_3I_4]$	0.33	138	*b*
$[PPh_3Me][Cu_3(AsPh_3)_3I_4]$	0.33	134	*b*

[s] r = Mole ratio of I^- to CuI in the complex. [b] This work.

Table 3. Comparison of core geometries in $[Cu_3(AsPh_3)_3I_4]^-$, $[Cu_4(AsPh_3)_4I_4]$, and $[Cu_4(PPh_3)_4I_4]$

Parameter[a]	$[AsPh_3Me]$ $[Cu_3(AsPh_3)_3I_4]$	'Cubane' $[Cu_4(AsPh_3)_4I_4]$[b]	'Cubane' $[Cu_4(PPh_3)_4I_4]$[c]
Cu–I	2.590(2)—2.755(3)	2.667(2)—2.724(2)	2.653(3)—2.732(3)
Cu–E	2.370(2)—2.394(3)	2.366(3)—2.384(3)	2.251(6)—2.258(7)
Cu · · · Cu	2.754(3)—2.885(4)	2.781(3)—2.900(3)	2.874(5)—3.164(4)
E–Cu–I	104.0(1)—115.0(1)	101.22(8)—112.06(9)	106.5(1)—116.9(2)
I–Cu–I	105.8(1)—116.9(1)	107.04(8)—114.53(8)	103.0(1)—115.0(1)
Cu–I–Cu	60.49(6)—65.69(9)	61.99(6)—65.72(7)	67.78(9)—71.75(9)

[a] Distances in Å, angles in °; E = As or P. [b] Ref. 13. [c] Ref. 14.

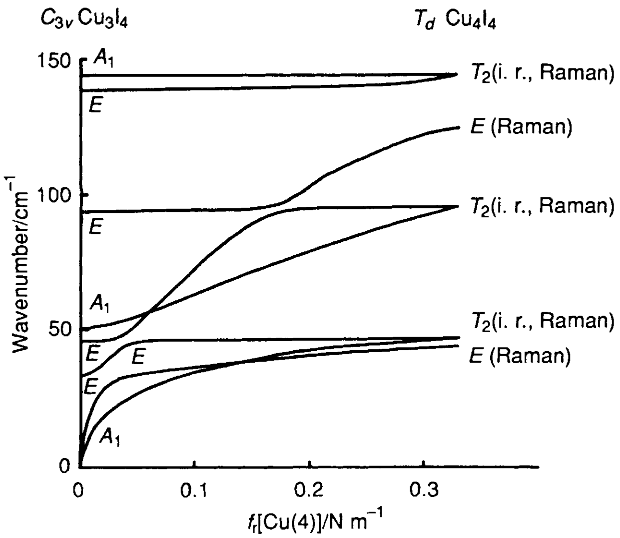

Figure 3. Correlation between the vibrational frequencies of C_{3v} Cu_3I_4 and T_d Cu_4I_4 clusters; f_r[Cu(4)] is the Cu–I bond-stretching force constant involving the fourth copper atom, which is removed in the transistion from Cu_4I_4 to Cu_3I_4

for the A_1 modes of the cluster. Thus, the simple analysis which accounts well for the relative positions of the vibrational bands of the Cu_4I_4 complexes seems also to account well for the form of the vibrational spectra of the Cu_3I_4 species.

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