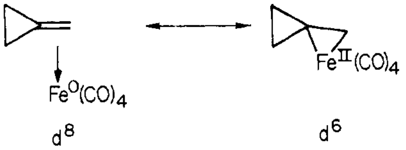
Table VI. Selected Nonbonded Intramolecular Distances (Å)

C(4)-C(9)	3.835	O(6)-C(9)	2.937
C(4)-C(13)	3.406	O(6)-C(13)	3.168
C(4)-O(10)	4.555	O(6)-O(10)	3.130
C(4)-O(14)	3.712	O(6)-O(14)	3.342
C(4)-Fe	3.235	O(6)-Fe	3.505

are more stable than those without.[16-18] Complex **2** contains two ester functions separated from the double bond by a cyclopropane ring, which might be expected to transmit electronic effects to the olefinic linkage reasonably effectively. The increased stability of electron-deficient olefin complexes is presumably due to the increased importance of the π-acceptor capabilities of the olefin ligand. In the case of **2**, another influence which increases the π-acceptor ability of the olefinic linkage is the strain associated with the incorporation of an sp^2 center in the three-membered ring. In valence-bond terms, increasing the π-acceptor component of the bond is equivalent to increasing the contribution of resonance structure **5b**. Associated with the contribution



5a **5b**

of this structure should be a distortion of the geometry of the ligand toward sp^3 hybridization at C(3) and a distortion of the coordination geometry at iron toward that characteristic of a d^6 complex (*i.e.*, octahedral). The considerable tilting of the three-membered ring away from the metal can be interpreted in terms of just such a distortion, magnified in this case by intramolecular repulsions between the ester groups and metal carbonyls. The enhanced importance of structure **5b** means that the methylenecyclopropane double bond is effectively a better π acceptor than a normal double bond. Because of the associated charge withdrawal from the metal the π-donor component of the C=C metal bond may be increased also, in order to maintain approximate charge neutrality in the system as a whole. Thus the total metal-C=C interaction is synergistically enhanced, and the complex substantially stabilized.

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Registry No. η^2-(*cis*-2,3-Dicarbomethoxymethylenecyclopropane)-iron tetracarbonyl, 51464-41-6.

Supplementary Material Available. Table I, a comparison of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1895.

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Molecules with an M_4X_4 Core. III.[1,2]
Comparison of the X-Ray Crystallographically Determined Molecular Structures of Tetrameric Triethylphosphinecopper(I) Iodide and Triethylarsinecopper(I) Iodide

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The crystal and molecular structure of tetrameric triethylphosphinecopper(I) iodide, $[PEt_3CuI]_4$, has been determined and that for tetrameric triethylarsinecopper(I) iodide, $[AsEt_3CuI]_4$ (originally studied by Wells in 1936) has been accurately redetermined. The species $[PEt_3CuI]_4$ crystallizes in the noncentrosymmetric cubic space group $I\bar{4}3m$ (T_d^3; No. 217) with $a = 13.024$ (1) Å and $Z = 2$; $[AsEt_3CuI]_4$ is both isomorphous and isostructural, with $a = 13.148$ (1) Å. For each species, X-ray diffraction data complete to $2\theta = 55°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved by conventional methods. Resulting discrepancy indices are $R_F = 3.48\%$ and $R_{wF} = 3.57\%$ for $[PEt_3CuI]_4$ (284 independent reflections) and $R_F = 4.07\%$ and $R_{wF} = 3.96\%$ for $[AsEt_3CuI]_4$ (295 independent reflections). Each of the tetrameric molecules lies on a site of T_d ($\bar{4}3m$) symmetry. The four copper and four iodine atoms, taken alternately, define the eight corners of a highly distorted "cubane" framework in which the Cu-I distance is 2.684 (1) Å for $[PEt_3CuI]_4$ and 2.677 (2) Å for $[AsEt_3CuI]_4$. The intramolecular Cu· · ·Cu distances are 2.927 (2) Å for $[PEt_3CuI]_4$ and 2.783 (2) Å (*in contrast* to the value of 2.60 Å reported by Wells) for $[AsEt_3CuI]_4$. While the Cu· · ·Cu distances in the two molecular species differ substantially, the intramolecular I· · ·I contacts are closely similar (I· · ·I = 4.380 (1) Å in $[PEt_3CuI]_4$ and 4.424 (2) Å in $[AsEt_3CuI]_4$).

Introduction

The crystal structure of tetrameric triethylarsinecopper(I) iodide, $[AsEt_3CuI]_4$, was originally reported by Wells in 1936;[3,4] the molecule was found to lie on a site of T_d ($\bar{4}3m$) symmetry and the (apparently nonbonding) copper· · ·copper distance was reported as 2.60 Å.[3,4]

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Recent structural studies on polynuclear copper cluster complexes have revealed a wide range of copper-copper distances, *viz.*, 2.377 (3)-2.389 (3) Å in tetrameric (4-methyl-2-cupriobenzyl)dimethylamine,[5] 2.417 Å in tetrameric trimethylsilylmethylcopper(I),[6] 2.48-2.70 Å in $[Cu(2\text{-}Me_2\text{-}NC_6H_4)]_4\cdot 2CuBr$,[7] 2.494 (6)-2.674 (5) Å in hexameric triphenylphosphinecopper(I) hydride,[8] 2.663 (6)-2.829 (6) Å in $(PPh_3Ir)_2Cu_4(C{\equiv}CPh)_8$,[9] 2.69 Å in $[Cu(S_2CNEt_2)]_4$,[10] 2.701-3.057 Å in $[Cu(SOCNPr_2)]_6$,[11] and 2.783-2.871 Å in $[Cu_8(S_2CC(CN)_2)_6{}^{4-}]$.[12] Bonding copper-copper interactions are claimed for distances up to 2.871 Å (in $[Cu_8(S_2CC(CN)_2)_6{}^{4-}]$).[12]

Recently we have reported the results of X-ray structural analyses of $[PPh_3CuCl]_4$ (a cubane-like molecule, in which Cu· · ·Cu = 3.1179 (13)-3.4298 (18) Å)[1,13] and $[PPh_3CuBr]_4\cdot 2CHCl_3$ (a molecule with a "step" configuration for its Cu_4Br_4 core, in which Cu· · ·Cu = 2.9905 (22)-3.9873 (23) Å),[2,13] and we have suggested that Wells' value of 2.60 Å for the Cu· · ·Cu vector in the cubane-like $[AsEt_3CuI]_4$ is of low precision. [This suggestion was based on the observations that the analysis was performed back in 1936, that a limited data set of 89 reflections was used, that parameters were not subjected to least-squares refinement, and that the copper atoms in the $[AsEt_3CuI]_4$ molecule are not the major contributors to the intensities of the Bragg reflections ($Z(\text{Cu}) = 29$, whereas $Z(\text{I}) = 53$ and $Z(\text{As}) = 33$).]

We now have completed a reinvestigation of the crystal structure of $[AsEt_3CuI]_4$ and have also completed an X-ray structural analysis of the related isomorphous and isostructural species $[PEt_3CuI]_4$. Our results are given below.

Experimental Section

Collection of Data for $[AsEt_3CuI]_4$. The compound $[AsEt_3CuI]_4$ was synthesized *via* the procedure of Mann, *et al.*[4] The crystal chosen for the analysis had a dodecahedral habit with well-formed {110} faces. Maximum and minimum distances between parallel pairs of faces were 0.32 and 0.12 mm.

A preliminary photographic study, using $h(0\text{-}2)l$ and $hk(0\text{-}2)$ precession photographs along with *b* and *c* cone-axis photographs (all taken with Mo Kα radiation), provided approximate unit cell parameters, revealed O_h ($m3m$) Laue symmetry for the diffraction pattern, and showed the systematic absences of hkl for $h + k + l = 2n + 1$. Possible space groups are $Im3$ [$T_h{}^5$; No. 204], $I432$ [O^5; No. 211], $I\bar{4}3m$ [$T_d{}^3$; No. 217], and $Im3m$ [$O_h{}^9$; No. 229]. The structure was successfully solved using the polar noncentrosymmetric space group $I\bar{4}3m$ (*vide infra*).

The crystal was centered on a Picker FACS-1 diffractometer and was aligned with its a^* axis coincident with the instrumental ϕ axis. Using "high-resolution conditions,"[14] the 2θ, ω, and χ settings of the resolved Mo Kα_1 peaks (λ 0.70930 Å) of 12 high-angle ($2\theta \approx 50°$) reflections were determined at 25 ± 1°. Least-squares refinement of the cell and orientation parameters yielded the unit cell parameter a = 13.1483 (14) Å. [This may be compared with Wells' value[3] of 13.08 ± 0.02 Å, measured, in the 1930's, at ambient temperatures in a Cambridge laboratory–*i.e.*, substantially *below* 25°!] The volume of the unit cell is 2273.05 Å^3; the calculated density is 2.060 g cm^{-3} (for mol wt 1410.226 and $Z = 2$), in keeping with the observed value of 2.05 g cm^{-3} reported by Wells.[3] For space group $I\bar{4}3m$, each molecule is required to be centered on a position of T_d ($\bar{4}3m$) symmetry.

Intensity data for reflections of the type $h + k + l = 2n$ in the range $0 < 2\theta \leqslant 55°$ and having positive h, k, and l indices (*i.e.*, six equivalent forms) were measured by executing a coupled θ(crystal)-2θ(counter) scan from 0.5° below the Mo Kα_1 peak to 0.5° above the Mo Kα_2. The experimental procedure has been described previously.[14] Details specific to the present analysis are as follows. (1) Mo radiation was filtered through an Nb filter of such thickness that ~47% of the Mo Kα radiation was transmitted; (2) scan speed was 0.5°/min; (3) background counting time was 40 sec each for low-angle and high-angle background; (4) takeoff angle was 3.0°; (5) detector aperture was 6 mm × 6 mm, 330 mm from the crystal.

During data collection the intensities of three standard reflections were measured after each batch of 48 reflections, in order to monitor possible decomposition or misorientation of the crystal. The root-mean-square deviations in the intensities of the check reflections were 1.03% for 220, 1.95% for 022, and 1.27% for 202; these deviations were reduced to 0.57, 0.83, and 0.67% (respectively) by assuming an (isotropic) linear decay throughout the data collection process.

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated as described previously,[14] using an "ignorance factor"[15] of 0.03. Any negative I was reset to zero; all data were retained, none being rejected on the basis of being "not significantly above background." All data were corrected for Lorentz, polarization, and absorption effects. With $\mu = 76.55$ cm^{-1}, the maximum and minimum transmission factors were 0.440 and 0.158. The validity of the absorption correction was confirmed by processing data from the strong axial 400 reflection, which had been measured, by a θ-2θ scan, at $\chi = 90°$ and at 10° intervals from $\phi = 0°$ to $\phi = 350°$. The 45% variation of intensity with ϕ was thereby reduced to approximately 4%.

Finally, equivalent reflections were averaged[16] and their intensity replaced by the σ^{-2} weighted average, with appropriately modified standard deviations. A total of 295 independent reflections were available for the subsequent analysis.

Collection of Data for $[PEt_3CuI]_4$. This species also was prepared by following the procedure of Mann, *et al.*[4] Maximum and minimum distances between parallel pairs of faces of the dodecahedral crystal were 0.21 mm and 0.07 mm, respectively. This complex is isomorphous with the analogous triethylarsine derivative. The course of the data collection and data reduction was essentially identical with that for $[AsEt_3CuI]_4$, save in the following respects.

(1) The unit cell dimension at 25 ± 1° was a = 13.0241 (11) Å. The unit cell volume was 2209.19 Å^3; observed and calculated densities were 1.84 ± 0.02 and 1.855 g cm^{-3} (for mol wt 1234.411 and $Z = 2$).

(2) Root-mean-square deviations in the intensities of the check reflections (220, 202, 022) were initially 1.85, 2.11, and 2.07%. These deviations were reduced to 0.61, 0.53, and 0.63% upon applying an isotropic linear decay correction to the entire data set.

(3) With a linear absorption correction of 49.216 cm^{-1}, the maximum and minimum transmission factors were 0.684 and 0.293. The validity of the absorption correction was confirmed by correcting the intensities measured for the axial 400 reflection at 10% increments of ϕ; the 38% variation in intensity was thereby reduced to ~3%.

(4) A total of 284 symmetry-independent reflections were obtained from one octant of data, *i.e.*, six equivalent forms [$2\theta_{\max} = 55°$; Mo Kα radiation].

Solution and Refinement of the Structures. Programs used in the structural determinations were as follows: FORDAP (Fourier synthesis, by A. Zalkin), LSHF (a much-modified version of SFLS5, by C. T. Prewitt, for structure factor calculations and full-matrix least-squares refinement of atomic parameters), STAN1 (calculation of distances and angles, with estimated standard deviations, by B. G.

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(16) Initially the hkl, lhk, and klh reflections were averaged, as were the khl, hlk, and lkh reflections. The two groups were then merged, the (unweighted) R factor for merging being 1.35% for the arsine complex. This confirms that the true Laue group is $m3m$, rather than $m3$. [The analogous R factor for the phosphine complex was 1.21%.]

DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson). Calculations were performed on an IBM 370/158 computer.

Scattering factors for neutral copper, arsenic, phosphorus, iodine, and carbon were taken from the compilation of Cromer and Waber;[17] both the real and imaginary components of anomalous dispersion were included in the calculations, using the values of Cromer and Liberman.[18] The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. Discrepancy indices used below are defined as

$$R_F = \frac{\Sigma ||F_o| - |F_c|| \times 100}{\Sigma |F_o|} \ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\ (\%)$$

The positions of copper, iodine, and arsenic atoms in $[AsEt_3CuI]_4$ were taken from the determination of Wells.[3] A three-dimensional Fourier synthesis, phased by these atoms, led to the location of the remaining nonhydrogen atoms. Least-squares refinement of positional and isotropic thermal parameters for the five crystallographically independent nonhydrogen atoms led to convergence with $R_F = 14.86\%$ and $R_{wF} = 20.69\%$. The use of anisotropic thermal parameters led to final convergence $[(\Delta/\sigma)_{max} < 0.025]$ with $R_F = 4.07\%$ and $R_{wF} = 3.96\%$ for the complete data set of 295 independent reflections.

Since $I\bar{4}3m$ is a noncentrosymmetric space group, there are two enantiomeric forms. The absolute configuration of the crystal was checked *via* the transformation of all atomic coordinates from (x, y, z) to $(-x, -y, -z)$ and refinement of parameters as before. Three cycles of least-squares refinement led to convergence with the increased residuals $R_F = 4.65\%$ and $R_{wF} = 4.90\%$. Clearly, the former coordinates (x, y, z) were the correct ones,[19] and the results of the latter refinement were discarded.

The final standard deviation in an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 2.82; the number of data (m) was 295 and the number of parameters was 25 $(m/n = 11.80)$. The function $\Sigma w(|F_o| - |F_c|)^2$ showed no significant dependence either upon $\sin\theta$ or upon $|F_o|$. The weighting scheme is thus valid, although it is not on an absolute scale. Data were inspected for evidence of secondary extinction or a "β-filter effect";[14] none was found. The correctness of the structure was confirmed unambiguously by means of a final difference-Fourier synthesis, on which the greatest features were peaks of height 0.47 e $Å^{-3}$ (at 0.680, 0.680, 0.680) and 0.39 e $Å^{-3}$ (at 0.620, 0.620, 0.720). Hydrogen atoms were not located.[20]

The crystal structure of $[PEt_3CuI]_4$ was solved by the trivial method of using the copper and iodine coordinates from the refined $[AsEt_3CuI]_4$ structure. A difference-Fourier synthesis led to the location of the other nonhydrogen atoms. Refinement of positional and isotropic thermal parameters converged at $R_F = 12.56\%$ and $R_{wF} = 18.46\%$. The use of anisotropic thermal parameters and incorporation of a secondary extinction correction led to final convergence $[(\Delta/\sigma)_{max} = 0.14]$ with $R_F = 3.48\%$ and $R_{wF} = 3.57\%$.

Inversion of the coordinates (x, y, z) to $(-x, -y, -z)$, as for the triethylarsine analog (*vide supra*), followed by three cycles of refinement, resulted in increased discrepancy indices $[R_F = 4.09\%$ and $R_{wF} = 4.07\%]$, indicating that the original choice of the crystal's chirality had been correct.

The function $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ had a value of 3.68 $(m = 284, n = 26, m/n = 10.92)$, indicating, again, a slight underestimation in the standard deviations assigned to the reflections. However, the weighting scheme gave residuals which were not significantly dependent upon θ or $|F_o|$. A final difference-Fourier synthesis had, as its three most prominent features, peaks of 0.62 e $Å^{-3}$ (at 0.50, 0.50, 0.56), 0.36 e $Å^{-3}$ (at 0.26, 0.26, 0.26), and 0.28 e $Å^{-3}$ (at 0.50, 0.50, 0.64). Hydrogen atoms of the ethyl groups were not located.[20]

Tables of observed and calculated structure factor amplitudes for $[AsEt_3CuI]_4$ and $[PEt_3CuI]_4$ are available.[21] Positional parameters for the two species are collected in Table I; anisotropic thermal parameters are shown in Table II. Intramolecular distances and angles, with their estimated standard deviations (esd's), are displayed in Table III.

Table I. Final Positional Parameters (with Esd's)[a] and "Equivalent Isotropic" Thermal Parameters[b]

Atom	Site symmetry	x	y	z	B, $Å^2$
		A. $[AsEt_3CuI]_4$			
Cu	$3m$	0.425176 (98)	$=x$	$=x$	5.68
I	$3m$	0.618954 (54)	$=x$	$=x$	5.64
As	$3m$	0.321495 (83)	$=x$	$=x$	6.03
C(1)[c]	1	0.3643 (20)	0.2947 (23)	0.1919 (19)	12.18
C(2)	m	0.3895 (13)	$=x$	0.1271 (18)	15.22
		B. $[PEt_3CuI]_4$[d]			
Cu	$3m$	0.420537 (86)	$=x$	$=x$	5.98
I	$3m$	0.618902 (46)	$=x$	$=x$	5.68
P	$3m$	0.32063 (19)	$=x$	$=x$	6.34
C(1)[c]	1	0.3665 (14)	0.2926 (15)	0.1962 (11)	8.70
C(2)	m	0.3870 (10)	$=x$	0.1320 (14)	15.16

[a] Esd's (estimated standard deviations), shown in parentheses, are right adjusted to the last digit of the preceding number. They are derived from the inverse of the final least-squares matrix. [b] The "equivalent isotropic" thermal parameters correspond to the average of the mean-square displacements along the three principal axes of the atomic vibration ellipsoid. [c] Atom C(1) is disordered about the mirror plane at (x, x, z). [d] Secondary extinction factor, β, was 0.81 (10) × 10^{-6}.

Some Comments on the Structural Determination of $[AsEt_3CuI]_4$ by Wells[3]

Table IV provides a direct comparison of the positional parameters for $[AsEt_3CuI]_4$ as determined originally by Wells with those determined in the present study. The following points should be made.

(1) Wells' report is essentially correct but is of relatively low precision.

(2) The x coordinates of the copper, iodine, and arsenic atoms were misplaced by only ~0.005, ~0.001, and ~0.001 (units of cell edge). Nevertheless, the error in the positioning of the copper atoms is sufficient for the reported Cu· · · Cu distance of 2.60 Å to be reduced by ~0.18 Å from its true value of 2.7826 (24) Å.

(3) The carbon atom positions deduced by Wells from packing considerations are erroneous. First, atom C(1) does not lie on the crystallographic mirror plane at (x, x, z) but is disordered about this plane, the two sites being (0.3643, 0.2947, 0.1919) and (0.2947, 0.3643, 0.1919). Second, the true coordinates for atom C(2) are (0.3895, 0.3895, 0.1271) rather than (0.30, 0.30, 0.10).

Discussion of the Molecular Geometry of $[AsEt_3CuI]_4$ and $[PEt_3CuI]_4$

These species have unit cells which contain two tetrameric molecules, each of which is centered on a site of crystallographic T_d $(\bar{4}3m)$ symmetry [at (0, 0, 0) and $(^1/_2, ^1/_2, ^1/_2)$—*i.e.*, Wyckoff position a of space group No. 217]. The individual tetrameric molecules are separated from their neighbors by normal van der Waals distances; there are no abnormally short contacts.

The geometry of the $As_4Cu_4I_4$ "core" of the $[AsEt_3CuI]_4$ molecule is shown in Figure 1. The $P_4Cu_4I_4$ core of $[PEt_3CuI]_4$ is similarly depicted in Figure 2. The complete molecular configurations of $[AsEt_3CuI]_4$ and $[PEt_3CuI]_4$, as viewed down their crystallographic S_4 $(\bar{4})$ axes, are shown in Figures 3 and 4 (respectively).

The Cu_4I_4 cores of the two molecules are defined by op-

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(20) Hydrogen atoms are subject to a twofold disorder (see text).

(21) See paragraph at end of paper regarding supplementary material.

Table II. Anisotropic Thermal Parameters with Esd's[a,b]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[c]
			(A) Parameters for $[AsEt_3CuI]_4$				
Cu	5.68 (5)	$=B_{11}$	$=B_{11}$	−0.79 (5)	$=B_{12}$	$=B_{12}$	0.23, 0.29, 0.29
I	5.64 (3)	$=B_{11}$	$=B_{11}$	−0.95 (3)	$=B_{12}$	$=B_{12}$	0.22, 0.29, 0.29
As	6.03 (5)	$=B_{11}$	$=B_{11}$	−1.12 (4)	$=B_{12}$	$=B_{12}$	0.22, 0.30, 0.30
C(1)	10.4 (15)	15.7 (25)	10.5 (14)	−7.1 (18)	−1.2 (11)	−5.4 (12)	0.19, 0.38, 0.53
C(2)	18.3 (18)	$=B_{11}$	9.1 (11)	−5.9 (22)	0.0 (9)	$=B_{13}$	0.34, 0.40, 0.55
			(B) Parameters for $[PEt_3CuI]_4$				
Cu	6.08 (5)	$=B_{11}$	$=B_{11}$	−0.70 (4)	$=B_{12}$	$=B_{12}$	0.24, 0.29, 0.29
I	5.75 (3)	$=B_{11}$	$=B_{11}$	−0.78 (2)	$=B_{12}$	$=B_{12}$	0.23, 0.29, 0.29
P	6.33 (9)	$=B_{11}$	$=B_{11}$	−0.90 (10)	$=B_{12}$	$=B_{12}$	0.24, 0.30, 0.30
C(1)	10.1 (10)	10.9 (11)	7.0 (7)	−2.5 (9)	−0.9 (7)	−2.8 (7)	0.25, 0.35, 0.41
C(2)	17.5 (14)	$=B_{11}$	8.5 (8)	−7.4 (16)	0.7 (6)	$=B_{13}$	0.32, 0.37, 0.56

[a] See footnote *a* to Table I. [b] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the calculated structure factor amplitude in the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [c] These values are the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see the figures.

Table III. Intramolecular Distances (in Å) and Angles (in deg) with Esd's[a,b]

$[AsEt_3CuI]_4$		$[PEt_3CuI]_4$	
	Distances		
Cu···Cu	2.7826 (24)	Cu···Cu	2.9272 (20)
I···I	4.4237 (15)	I···I	4.3800 (11)
Cu-I	2.6767 (15)	Cu-I	2.6837 (13)
Cu···I	4.4130 (16)	Cu···I	4.4748 (14)
Cu-As	2.3612 (17)	Cu-P	2.2538 (27)
As-C(1)	1.829 (27)	P-C(1)	1.766 (15)
C(1)-C(2)	1.545 (28)	C(1)-C(2)	1.510 (21)
C(1)···C(1′)	1.295 (68)	C(1)···C(1′)	1.360 (45)
	Angles		
I-Cu-I	111.45 (5)	I-Cu-I	109.38 (4)
I-Cu-As	107.41 (6)	I-Cu-P	109.56 (8)
Cu-I-Cu	62.63 (5)	Cu-I-Cu	66.10 (4)
Cu-As-C(1)	118.1 (13)	Cu-P-C(1)	117.0 (10)
C(1)-As-C(1)*[c]	99.6 (7)	C(1)-P-C(1)*[c]	101.0 (6)
As-C(1)-C(2)	115.1 (19)	P-C(1)-C(2)	113.6 (13)

[a] Esd's were calculated by considering the full correlation matrix. The calculation was performed using the FORTRAN IV program STAN1, by B. G. DeBoer. Errors in the unit cell dimensions were included. [b] Bond lengths were not corrected for the effects of thermal motion. [c] C(1)* is related to C(1) by a C_3 rotation about the Cu-As or Cu-P axis.

Table IV. Comparison of the Positional Parameters from the Wells[a] and Churchill-Kalra Determinations of the Structure of $[AsEt_3CuI]_4$

Parameters	Wells[a]	Churchill-Kalra[b]
x(Cu)	0.430	0.425176 (98)
x(I)	0.120 [≡0.620]	0.618954 (54)
x(As)	0.320	0.321495 (83)
x(C(1))	0.365[c]	0.3643 (20)
y(C(1))		0.2947 (23)
z(C(1))	0.18[c]	0.1919 (19)
x(C(2))	0.30[c]	0.3895 (13)
z(C(2))	0.10[c]	0.1271 (18)

[a] See ref 3. [b] See Table I for further details. [c] These positions were deduced from packing considerations. The carbon atoms were not located directly.

posed, interpenetrating, concentric Cu_4 and I_4 tetrahedra; the arrangement of copper and iodine atoms thus obtained is best described as a highly distorted "cubane" configuration of precise (*i.e.*, crystallographically dictated) T_d symmetry. The copper-iodine bond distances in the two complexes are nearly identical, with values of 2.6837 (13) Å for $[PEt_3CuI]_4$ and 2.6767 (15) Å for $[AsEt_3CuI]_4$, the difference being only 0.0070 (20) Å.[22]

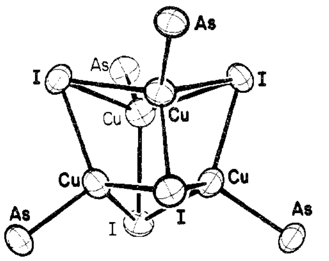

Figure 1. The $As_4Cu_4I_4$ core of the $[AsEt_3CuI]_4$ molecule (ORTEP diagram, 30% probability ellipsoids).

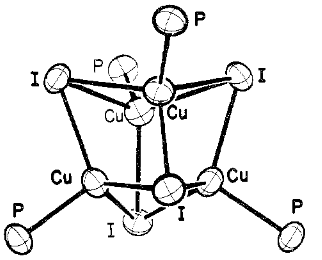

Figure 2. The $P_4Cu_4I_4$ core of the $[PEt_3CuI]_4$ molecule.

Copper···copper distances in the two complexes are, however, widely different, with values of 2.9272 (20) Å for $[PEt_3CuI]_4$ and 2.7826 (24) Å for $[AsEt_3CuI]_4$. The difference of 0.1446 (31) Å[22] corresponds to 47σ! It is clear from other work that nonbonding intracluster copper···copper interactions are extremely "soft." [Thus, Cu···Cu distances in the "cubane" species $[PPh_3CuCl]_4$[1] range from 3.1179 (13) to 3.4298 (18) Å; also, the Cu···Cu distance of 3.14 Å in the solvated binuclear species $(Ph_3P)_2Cu(\mu\text{-}Cl)_2Cu(Ph_3P)\cdot C_6H_6$[23] is ~0.23 Å longer than that of 2.909 (2) Å in the otherwise identical, but *nonsolvated*, species $(Ph_3P)_2Cu(\mu\text{-}Cl)_2Cu(Ph_3P)$.[24]]

There is considerable evidence to indicate that the disparity between the copper···copper distances of $[PEt_3CuI]_4$ and $[AsEt_3CuI]_4$ owes its origin to a combination of nonbonding interactions.

(1) Iodine···iodine contacts within the two species differ by only 0.0437 (19) Å, individual values being 4.3800 (11) Å in $[PEt_3CuI]_4$ and 4.4237 (15) Å in $[AsEt_3CuI]_4$. While the difference is highly significant in a statistical sense (corresponding to ~23σ), it is, both numerically and percentage-

(22) $\sigma(\text{diff}) = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$.

(23) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, 92, 3805 (1970).

(24) V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972).

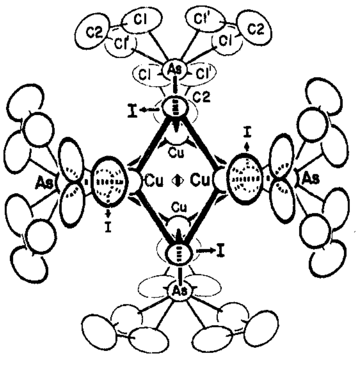

Figure 3. The $[AsEt_3CuI]_4$ molecule viewed along its S_4 ($\bar{4}$) axis.

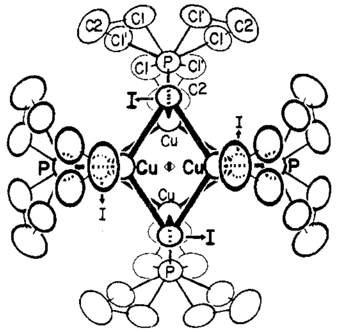

Figure 4. The $[PEt_3CuI]_4$ molecule viewed along its S_4 ($\bar{4}$) axis.

wise, considerably smaller than the difference found for the copper· · ·copper contacts. Furthermore, the observed I· · ·I distances are extremely close to the value expected for a normal van der Waals contact. (The van der Waals radius for iodine is approximately 2.15 Å.[25]) This suggests that iodine· · ·iodine repulsions essentially dictate a lower limit for the overall "molecular size" of $[PEt_3CuI]_4$ and $[AsEt_3CuI]_4$.

(2) The $Cu(\mu\text{-}I)_2Cu$ faces of the cubane framework are decidedly nonplanar and the dihedral angles between I-Cu-I planes are "soft" and are easily deformed by intermolecular forces. Within these $Cu(\mu\text{-}I)_2Cu$ faces, the dihedral angles about the I· · ·I axes are 134.72° for $[AsEt_3CuI]_4$ as opposed to 141.32° for $[PEt_3CuI]_4$, while dihedral angles about the Cu· · ·Cu vectors are 150.60° for $[AsEt_3CuI]_4$ and 153.60° for $[PEt_3CuI]_4$ (see Table V).

(3) The unit cell edge of 13.1483 (14) Å for $[AsEt_3CuI]_4$ is only 0.1242 (18) Å, or about 1% greater than that of 13.0241 (11) Å for $[PEt_3CuI]_4$. Since the covalent radius for arsenic is 1.21 Å, as opposed to a value of 1.10 Å for phosphorus,[26] it is clear the *small* expansion of the cell of $[AsEt_3CuI]_4$ *vis a vis* $[PEt_3CuI]_4$ is the net result of the increased size of As (*vs.* P) being compensated, in part, by a compression in the Cu_4 tetrahedron in $[AsEt_3CuI]_4$ relative to that in $[PEt_3CuI]_4$. In keeping with this, a contraction in ∠AsCuI *vs.* ∠PCuI is observed, with values of 107.41 (6) and 109.56 (8)°, accompanied by a corresponding expansion of the angles I-Cu-I (111.45 (5)° for $[AsEt_3CuI]_4$, as opposed to 109.38 (4)° in $[PEt_3CuI]_4$). The observed Cu-As and Cu-P bond lengths are 2.3612 (17) and 2.2538 (27) Å, respectively. The As-C(1) and P-C(1) distances are 1.829 (27) and 1.766 (15) Å; it should be emphasized, however, that these latter distances are of limited accuracy because of the disorder of C(1) about the crystallographic mirror plane.

Table V. Planes and Dihedral Angles[a]

Atom	Dev, Å	Atom	Dev, Å
(A) $[AsEt_3CuI]_4$			
Plane I: $0.27217X + 0.27217Y + 0.92295Z = 8.2027$			
Cu(*x*, *x*, *x*)*	0.000	Cu(1 − *x*, 1 − *x*, *x*)	+1.071
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane II: $-0.27217X - 0.27217Y + 0.92295Z = 1.0455$			
Cu(1 − *x*, 1 − *x*, *x*)*	0.000	Cu(*x*, *x*, *x*)	+1.071
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane III: $-0.17942X + 0.17942Y + 0.96727Z = 5.4074$			
Cu(*x*, *x*, *x*)*	0.000	I(*x*, 1 − *x*, 1 − *x*)	−1.123
Cu(1 − *x*, 1 − *x*, *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane IV: $0.17942X - 0.17942Y + 0.96727Z = 5.4074$			
Cu(*x*, *x*, *x*)*	0.000	I(1 − *x*, *x*, 1 − *x*)	−1.123
Cu(1 − *x*, 1 − *x*, *x*)*	0.000		
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
Dihedral Angles: I-II = 134.72°; III-IV = 150.60°			
(B) $[PEt_3CuI]_4$			
Plane I: $0.23416X + 0.23416Y + 0.94358Z = 7.7331$			
Cu(*x*, *x*, *x*)*	0.000	Cu(1 − *x*, 1 − *x*, *x*)	+0.969
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane II: $-0.23416X - 0.23416Y + 0.94358Z = 1.6337$			
Cu(1 − *x*, 1 − *x*, *x*)*	0.000	Cu(*x*, *x*, *x*)	+0.969
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane III: $-0.16147X + 0.16147Y + 0.97358Z = 5.3324$			
Cu(*x*, *x*, *x*)*	0.000	I(*x*, 1 − *x*, 1 − *x*)	−1.000
Cu(1 − *x*, 1 − *x*, *x*)*	0.000		
I(1 − *x*, *x*, 1 − *x*)*	0.000		
Plane IV: $0.16147X - 0.16147Y + 0.97358Z = 5.3324$			
Cu(*x*, *x*, *x*)*	0.000	I(1 − *x*, *x*, 1 − *x*)	−1.000
Cu(1 − *x*, 1 − *x*, *x*)*	0.000		
I(*x*, 1 − *x*, 1 − *x*)*	0.000		
Dihedral Angles: I-II = 141.32°; III-IV = 153.60°			

[a] Cartesian coordinates (*i.e.*, $X = ax$, $Y = ay$, $Z = az$). Only atoms marked with an asterisk were used in the calculation of the plane. Calculations were performed using the program PLOD, by B. G. DeBoer.

The Cu(+I) atoms are each in an environment of precise C_{3v} symmetry, with coordination angles ∠ICuI = 111.45 (5)° and ∠AsCuI = 107.41 (6)° for $[AsEt_3CuI]_4$ and ∠ICuI = 109.38 (4)° and ∠PCuI = 109.56 (8)° for $[PEt_3CuI]_4$.

One slightly disturbing feature is the small value found for Cu-I-Cu angles—*viz.*, 62.63 (5)° for $[AsEt_3CuI]_4$ and 66.10 (5)° for $[PEt_3CuI]_4$. While M-X-M angles less than 90° are generally regarded as signifying metal-metal bonding in $(\mu\text{-}X)_2$-bridged *octahedral and square-planar* complexes, this generalization does not carry over into species containing metals with a tetrahedral coordination geometry.

The contraction of the Cu-I-Cu angles to values of 62.63 (5) and 66.10 (5)° is thus explained as the result of a combination of (i) requirement of a regular tetrahedral value of ~109.5° for the I-Cu-I angle (found: 111.45 (5) and 109.38 (5)° for As- and P-containing complexes, respectively) and (ii) compression of the Cu_4 tetrahedron as a result of crystal packing (*vide supra*). It is *not* necessary to invoke direct copper-copper bonding.

The geometry of the triethylpnicogen ligands is as expected. The phosphorus and arsenic atoms lie at positions of precise C_3 symmetry. Angles about arsenic are Cu-As-C(1) = 118.1 (13)° and C(1)-As-C(1)* = 99.6 (7)°, while those about phosphorus are Cu-P-C(1) = 117.0 (10) and C(1)-P-C(1)* = 101.0 (6)°. The contraction of C-P-C and C-As-C angles in

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(25) L. Pauling "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

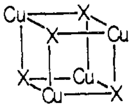
(26) See ref 25, p 224.

M-(P or As)R_3 species from a regular tetrahedral value is, of course, a well-known phenomenon.[27]

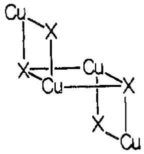
Finally we may note that the C(1)-C(2) distances are 1.545 (28) Å in $[AsEt_3CuI]_4$ and 1.510 (21) Å in $[PEt_3CuI]_4$.

A Survey of Species with a $P_4Cu_4X_4$ or $As_4Cu_4X_4$ Core

To date crystallographic studies on five of these species have been reported. $[PPh_3CuCl]_4$[1], $[PEt_3CuI]_4$, and $[AsEt_3CuI]_4$ each have the cubane skeleton (I), while $[PPh_3CuBr]_4$[2] and $(Ph_2PCH_2PPh_2)_2Cu_4I_4$[28] each possess a "step" skeleton (II).



I



II

The factors governing the stability of one skeletal form over another have been listed previously,[2] but it is still not possible to *predict* which structure will be of lowest energy, or to determine the difference in energy between the two forms, for a given molecular stoichiometry. Further studies are under way in an effort to resolve some of these problems.

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Registry No. $[AsEt_3CuI]_4$, 51364-97-7; $[PEt_3CuI]_4$, 51364-98-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1899.

(27) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968); see, especially, Table 7 on p 2976.

(28) M. Marsich, G. Nardin, and L. Randaccio, *J. Amer. Chem. Soc.*, 95, 4053 (1973).

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Synthesis and Crystal Structure of a Dimeric Cyclic Copper(I)-Aliphatic Disulfide Complex: *cyclo*-Di-μ-{bis[2-(*N*,*N*-dimethylamino)ethyl] disulfide}-dicopper(I) Tetrafluoroborate

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The compound *cyclo*-di-μ-{bis-[2-(*N*,*N*-dimethylamino)ethyl] disulfide}-dicopper(I) tetrafluoroborate, alternatively named *cyclo*-di-μ-{2,2′-dithiobis[*N*,*N*-dimethyl]ethylamino}-dicopper(I) tetrafluoroborate, $Cu_2((CH_3)_2NCH_2CH_2SSCH_2CH_2N(CH_3)_2)_2(BF_4)_2$, was synthesized by direct reaction between Cu(I) and the disulfide ligand and also by disulfide ligand reduction with Cu(II) and subsequent Cu(I) coordination with excess disulfide. Its crystal structure has been determined by single-crystal X-ray diffraction techniques. After nearly full-matrix least-squares refinement using anisotropic thermal parameters only for atoms heavier than carbon, the conventional *R* index converged at 0.063. The yellow crystals form in the noncentric orthorhombic space group $Pn2_1a$ with $a = 28.763$ (8), $b = 11.451$ (2), and $c = 9.293$ (4) Å. Two ligand molecules coordinate to each of two Cu(I) ions, forming a dipositive complex cation with a central six-membered CuSSCuSS ring in a twisted-boat conformation. A very approximate twofold axis is normal to the best plane through that ring. Four strained CuSCCN rings share an edge with the central ring; the coordination of Cu(I) is badly distorted tetrahedral with angles varying from 89.6 to 123.9°. The length of the disulfide bond and the CSSC dihedral angle are altered by complexation, as compared to the values observed in the structure of the relatively unconstrained hydrochloride salt, as are the CS and SS stretching frequencies, as determined by infrared and laser-Raman methods. The bond length has increased from 2.037 (1) to 2.075 (6) Å and the dihedral angle has increased from 82.4 (4) to 106.3 (9)°. The Cu(I)-S bond lengths are short, averaging 2.30 Å, and the average Cu(I)-N bond is 2.13 Å. The perchlorate salt of the same complexed cation is isostructural.

Introduction

A host of metalloproteins and metalloenzymes contain Cu(I) or Cu(II) ions which are necessary for their function.[1,2] These ions can also act as enzymatic inhibitors[2] and are useful as specific reagents in protein analysis.[3] The metalloproteins hemocyanin[4] and tyrosinase[1] (phenol oxidase) contain copper ions which undergo cyclic redox processes *in vivo*. Some proteins such as neonatal hepatic mitochondrocuprein have unusually high copper and cysteine contents,[2] which suggest important copper-sulfur interactions. Although Cu(II) is usually associated with oxygen and nitrogen, and occasionally sulfur ligands in protein structure, Cu(I) is more likely to coordinate to sulfur-containing groups. In response to the suggestion that ligands such as organic disulfides might behave "noninnocently"[5] in redox processes by direct participation involving delocalized orbitals, we have chosen to investigate aliphatic disulfide complexes of Cu(I).

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(2) B. L. Vallee and W. E. C. Wacker, *Proteins*, 5, 41-60, 83, 143-146 (1970).

(3) R. A. Phelps, K. A. Neet, L. T. Lynn, and F. W. Putnam, *J. Biol. Chem.*, 236, 96 (1961).

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