Synthesis, Crystal and Molecular Structure of Di-μ-chlorotetrakis(triphenylarsine)dicopper(I), $[\{(C_6H_5)_3As\}_2CuCl]_2 \cdot 2CDCl_3$

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Copper(I) halides form complexes with electron-pair donor ligands such as phosphines, arsines, and nitrogen bases, which show a variety of structural features in the solid state.[1-4] The stoichiometry of copper(I) complexes varies in several ways such as L_3CuX, L_2CuX, $L_{1.5}CuX$, LCuX, and etc. (L=PR_3; AsR_3; N-donor ligands, X=Cl; Br; I). Complexes of copper(I) halides with phosphorus and arsenic ligands of general formula $(MXL_2)_2$ and MXL_2 have been studied structurally.[5-10]

In this paper we report the synthesis and molecular structure of a novel copper(I) dimer bridged by two chlorine atoms, $[\{(C_6H_5)_3As\}_2CuCl]_2 \cdot 2CDCl_3$, having a general formula $(MXL_2)_2$, where in our work the ligand L is the triphenylarsine and X the chloro ligand.

Experimental

Materials. $[\{(C_6H_5)_3As\}_2CuCl]_2$ was synthesized by $CuCl_2 \cdot 2H_2O$ (1 mmol, 71 mg) and triphenylarsine (1.5 mmol, 459 mg) in 30 mL of ethanol. The reaction mixture was refluxed for 12 hr and was then cooled to room temperature. The white power formed was filtered and dissolved in 20 mL of chloroform. The solution was filtered to remove any solid materials. 10 mL of n-pentane was added to the filtrate. At this point, the solution became cloudy.

The solution was filtered and the filtrate was stored in a refrigerator maintained at 20 °C for 2 days. The white precipitates formed were filtered and were washed with ethyl ether. Yield: 330 mg (20%). The product is very stable in air. However, the product, when dissolved in chloroform containing n-pentane, decomposes after about 10 days in air.

X-ray data collection and refinement. A crystal of $[\{(C_6H_5)_3As\}_2CuCl]_2 \cdot 2CDCl_3$ suitable for X-ray analysis was grown by dissolving the white powder in $CDCl_3$ and by layering n-pentane in a 5 mm NMR tube in air at *ca.* −20 °C. Large colorless transparent crystals were readily formed in the tube after a day.

A crystal (0.45×0.45×0.50 mm) was sealed in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer equipped with a monochromator and molybdenum radiation. Unit cell dimensions were determined by least-squares refinement of 25 intense reflections ($2.98<2\theta<49.94$). Data were collected at ambient temperature [293 (2) K] in $\omega/2\theta$ scan mode using variable rates for the range $0 \leq h \leq 24$, $0 \leq k \leq 21$, $-22 \leq l \leq 22$, and three standard reflections measured after every hour did not reveal any systematic variations in intensity. 2943 reflections were collected, 2844 unique intensities observed. Intensities were corrected for Lorentz and polarization effects but not for absorption.

The crystal structure was determined by the conventional heavy atom method and Fourier techniques. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were located in the calculated positions. All the calculations were performed on IBM PC 486 computer using SHELXS[5] and SHELXL-93[6] and atomic scattering factors for all nonhydrogen atoms were supplied by the SHELXS-86 system. Crystal parameters and procedural information corresponding to data collection and structure refinement are collected in Table 1.

Table 1. Crystal data and structure refinement for $[\{(C_6H_5)_3As\}_2CuCl]_2 \cdot 2CDCl_3$

Empirical formula	$C_{72}H_{60}As_4Cl_2Cu_2 \cdot 2CDCl_3$
Formula weight	1661.71
Temperature, K	293 (2)
Crystal system	Monoclinic
Space group	*C2/c* (No. 15)
a, Å	21.251 (4)
b, Å	17.877 (3)
c, Å	19.288 (4)
β, deg	91.81 (2)
V, $Å^3$	7324
Z	4
d_{calc}, g/cm^3	1.507
Radiation	graphite monochromated Mo Kα
Wavelength, Å	0.71073
Absorption coefficient, mm^{-1}	2.706
F(000)	3328
Crystal size, mm	0.45×0.45×0.50
θ range for data collection	1.49 to 24.97 deg.
Index ranges	$0 \leq h \leq 24$, $0 \leq k \leq 21$, $-22 \leq l \leq 22$
Reflections collected	2943
Independent reflections	2844 [R(int)=0.0235]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2844/0/386
Goodness-of-fit on F^2	0.967
Final R indices [$I>2\sigma(I)$]	R_1=0.0595, wR_2=0.1478
R indices (all data)	R_1=0.0638, wR_2=0.1522
Largest diff. peak and hole, e.$Å^{-3}$	1.028 and −0.616

$R_1=\Sigma||Fo|-|Fc||/\Sigma|Fo|$. $wR_2=\{\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4\}^{1/2}$, where $w=1/\{\sigma^2Fo^2+(aP)^2+bP\}$, $P=\{Max(Fo^2, 0)+2Fc^2\}/3$ and a, b were determined by the program.

Results and Discussion

Copper(I) complexes can be obtained by a reduction reaction of copper(II) complexes in the presence of excess PR_3 and AsR_3 acting as a reducing agent.[1] The stoichiometry and chemistry of copper(I) and analogous silver(I) compounds containing both halogen bridges and terminal phosphine or arsenic ligands are delicately dependent on the kind of the bridging halogen atoms as well as the type of phosphine or arsenic ligands,[7-11] though, in general, there is no strict rules governing the geometry.

The stoichiometry of LCuX and LAgX corresponding to the tetrameric (phosphine or arsine) copper(I) halides and (phosphine or arsine) silver(I) halides usually have two possible geometrically different structures: cubane-like and chair-like (sometimes called step-like) tetrameric isomers. For example, both $[(Et_3As)CuI]_4$ and $[\{(C_6H_5)_3As\}CuI]_4$ have been found as the cubane-like isomer,[7,8] while the chair-like structure is observed for $[\{(C_6H_5)_3P\}CuBr]_4$[12] and $[\{(C_6H_5)_3P\}CuI]_4$.[13] On the other hand, both the cubane-like and the chair-like structures have been characterized for $[\{(C_6H_5)_3P\}AgI]_4$.[11]

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2\times 10^3$) for non-hydrogen atoms of $[\{(C_6H_5)_3As\}_2CuCl]_2\cdot 2CDCl_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	U_{eq}
Cu	4273(1)	7582(1)	2572(1)	46(1)
Cl(1)	5000	6580(2)	2500	57(1)
Cl(1)'	5000	8581(2)	2500	51(1)
As(1)	3643(1)	7582(1)	1522(1)	45(1)
As(2)	3683(1)	7583(1)	3598(1)	43(1)
C(1)	3085(7)	8422(7)	1391(7)	54(4)
C(2)	3015(10)	8893(10)	1947(8)	106(7)
C(3)	2614(14)	9520(12)	1886(11)	168(13)
C(4)	2313(10)	9655(9)	1246(11)	105(7)
C(5)	2418(8)	9221(9)	706(9)	76(5)
C(6)	2812(7)	8630(8)	770(7)	69(4)
C(7)	3096(6)	6708(7)	1415(6)	44(3)
C(8)	3337(7)	6022(7)	1575(7)	55(4)
C(9)	2970(8)	5395(8)	1515(8)	69(4)
C(10)	2355(8)	5455(9)	1276(8)	71(5)
C(11)	2106(7)	6125(8)	1128(7)	65(4)
C(12)	2465(7)	6761(8)	1184(7)	64(4)
C(13)	4028(5)	7580(8)	629(6)	49(3)
C(14)	4490(6)	8084(8)	494(7)	65(4)
C(15)	4758(7)	8129(10)	-138(9)	86(5)
C(16)	4595(8)	7631(12)	-646(8)	104(7)
C(17)	4134(9)	7094(10)	-529(8)	95(6)
C(18)	3860(7)	7075(10)	119(8)	76(5)
C(19)	2776(5)	7528(7)	3426(5)	44(3)
C(20)	2546(6)	6921(8)	3080(6)	52(3)
C(21)	1911(7)	6840(10)	2907(8)	81(5)
C(22)	1504(8)	7412(12)	3105(9)	98(6)
C(23)	1733(7)	8009(11)	3464(10)	98(6)
C(24)	2365(6)	8069(8)	3614(9)	74(5)
C(25)	3743(6)	8429(7)	4234(7)	48(3)
C(26)	3502(7)	8406(8)	4891(7)	60(4)
C(27)	3557(7)	9023(9)	5318(8)	69(4)
C(28)	3862(7)	9658(9)	5101(8)	72(5)
C(29)	4119(7)	9664(8)	4471(8)	67(4)
C(30)	4054(6)	9063(7)	4034(7)	52(3)
C(31)	3804(6)	6733(7)	4219(6)	45(3)
C(32)	3320(7)	6430(8)	4600(7)	61(4)
C(33)	3430(9)	5836(8)	5026(8)	70(5)
C(34)	4009(10)	5543(10)	5085(9)	94(6)
C(35)	4497(8)	5832(10)	4732(10)	105(7)
C(36)	4401(8)	6431(9)	4289(8)	78(5)
Cl(3)[†]	4566(7)	576(9)	1703(8)	172(6)
Cl(4)[†]	5763(8)	621(10)	2249(9)	192(6)
Cl(5)[†]	5312(6)	1027(7)	1891(7)	138(4)
Cl(6)[†]	4740(5)	4318(6)	1753(6)	183(4)
Cl(7)[†]	5818(8)	4470(10)	2143(9)	307(8)
C(1)[†]	5000	430(12)	2500	78(7)
C(2)[†]	5000	4662(21)	2500	157(14)

Symmetry transformations used to generate equivalent atoms: -x+1, y, -z+1/2. Solvate molecules.

The coexisting two isomers of $[\{(C_6H_5)_3P\}AgI]_4$ give the very useful information about the possible transformation of the highly distorted cubane-like isomer to the less stressed chiar-like isomer owing to the intramolecular van der Waals repulsions involving the bulky terminal ligands and the bridging halides. Moreover, sometimes the tetrameric complex undergoes cleavage to a dimeric complex by good coordinating solvent like acetonitrile. $[\{(C_6H_5)_3As\}CuI]_4$ was cleaved by acetonitrile to form dimeric $[\{(C_6H_5)_3As\}(MeCN)CuI]_2$, which have been confirmed by a single-crystal X-ray diffraction study by Churchill and Missert.[9] In case of the stoichiometry L_2CuX, the above-mentioned structure with tetrahedral dimeric geometry is common. It seems probable that the preference for L_2MX dimeric stoichiometry relative to LMX tetrameric one must have something to do with the size of L and X as previously pointed out by Lippard.[2]

Triphenylarsine reacted with $CuCl_2\cdot 2H_2O$ (molar ratio 1.5 : 1) in refluxing ethanol for 12 h. As shown in the work by the Healy group, the nature of the copper(I) halide ggregation with bases in solution is very complex and variable.[3] However, in this work the dinuclear species **1** having chlorine bridges has been nicely isolated as pure colourless single crystals suitable for X-ray diffraction study. The crystal structure of solvated $\mathbf{1}\cdot 2CDCl_3$ has been unequivocally confirmed by X-ray diffraction. The crystal of complex **1** consists of discrete molecular units of the dimeric species $\{(C_6H_5)_3As\}_2CuCl]_2$ which are separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. Selected interatomic distances and angles for $\mathbf{1}\cdot 2CDCl_3$ are collected in Table 3. A perspective

Table 3. Selected interatomic distances (Å) and angles (deg) for $[\{(C_6H_5)_3As\}_2CuCl]_2\cdot 2CDCl_3$

Cu(1)-As(1)	2.391(2)	As(2)-C(19)	1.948(11)
Cu(1)-As(2)	2.376(2)	As(2)-C(25)	1.949(13)
Cu(1)-Cl(1)	2.373(4)	As(2)-C(31)	1.946(12)
Cu(1)-Cl(2)	2.369(4)	Cu(1)···Cu(1)'	3.113(4)
As(1)-C(1)	1.923(13)	Cl(1)···Cl(2)	3.578(6)
As(1)-C(7)	1.955(12)	C-C(Ph, avg.)	1.37(2)
As(1)-C(13)	1.931(11)		
As(1)-Cu(1)-As(2)	114.18(7)	Cu(1)-As(1)-C(13)	99.3(5)
As(1)-Cu(1)-Cl(1)	107.42(7)	Cu(1)-As(2)-C(19)	113.8(3)
As(1)-Cu(1)-Cl(2)	107.42(7)	Cu(1)-As(2)-C(25)	119.9(4)
As(1)-Cu(1)-Cu(1)'	117.16(7)	Cu(1)-As(2)-C(31)	116.7(4)
As(2)-Cu(1)-Cl(1)	114.23(8)	C(1)-As(1)-C(7)	104.4(5)
As(2)-Cu(1)-Cl(2)	114.21(8)	C(1)-As(1)-C(13)	99.3(5)
As(2)-Cu(1)-Cu(1)'	128.67(8)	C(7)-As(1)-C(13)	99.9(5)
Cl(1)-Cu(1)-Cl(2)	97.96(11)	C(19)-As(2)-C(25)	101.0(5)
Cu(1)-Cl(1)-Cu(1)'	82.0(2)	C(19)-As(2)-C(31)	100.1(5)
Cu(1)-As(1)-C(1)	116.0(4)	C(25)-As(2)-C(31)	102.4(5)
Cu(1)-As(1)-C(7)	113.9(4)		

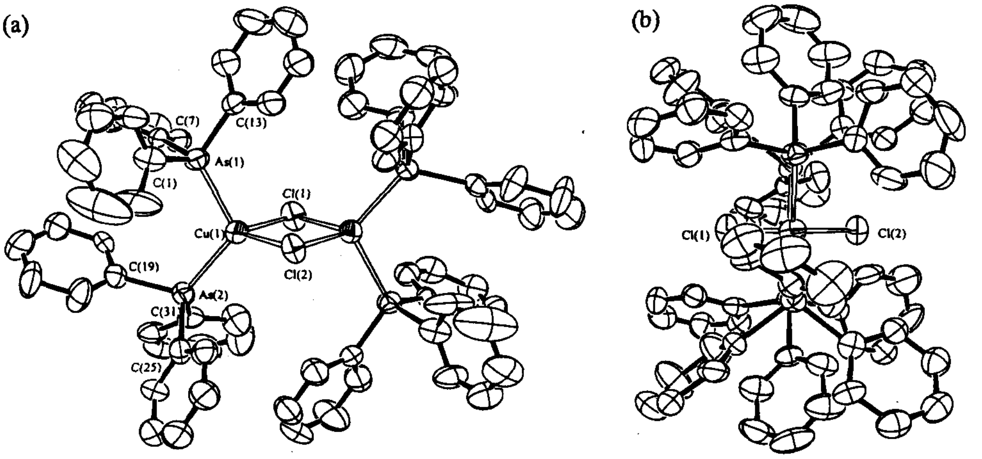

Figure 1. ORTEP (50% probability) views of $[\{(C_6H_5)_3As\}_2CuCl]_2\cdot 2CDCl_3$ with main atom numbering, a front view (a) and a side view (b). Hydrogen atoms and solvated two $CDCl_3$ molecules are omitted for clarity.

view of complex 1 with atom-numbering appears in Figure 1 and the core of the molecule in Figure 2.

The copper(I) centers are in pseudo-tetrahedral environments and are connected via two bridging chlorine atoms [Cu(1)-Cl(1)=2.373(4) Å, Cu(1)-Cl(2)=2.369(4) Å] Aso, each copper(I) atom is bonded asymmetrically to two triphenylarsine ligands [Cu(1)-As(1)=2.391(2) Å, Cu(1)-As(2)= 2.376(2) Å]. The Cu_2Cl_2 core planar, with a intramolecular Cu(1) ··· Cu(1)' distance of 3.113(4) Å and a Cl(1) ··· Cl(2) distance of 3.578(6) Å, represents no direct interactions between two copper atoms and between two chlorine atoms, respectively. Two disordred solvent $CDCl_3$ molecules are located above and below the Cu_2Cl_2 plane in the middle of two asymmetric triphenylarsine ligands but they are eliminated in Figure 1 for the sake of clarity.

The structure in Figure 1 and Figure 2 has a crystallographic twofold rotation axis with Cl(1) ··· Cl(2) axis that requires Cu_2Cl_2 moiety to be strictly planar. The most interesting feature is that (1) the As(1)-Cu(1)-Cl(1) angle and the As(1)-Cu(1)-Cl(2) angle are same with 107.42(7)°, and (2) the As(2)-Cu(1)-Cl(1) angle and the As(2)-Cu(1)-Cl(2) angle are same with being 114.41(8)°. So the angle between As(1)-Cu(1)-As(2) plane and Cl(1)-Cu(1)-Cl(2) plane is exactly 90°. Except Cu(1)-As(1)-C(13) [99.3(5)°], all the Cu-As-C(ipso) angles are larger than the regular tetrahedral angle of 109.47°, with values ranging from 113.8 (3)° to 119.

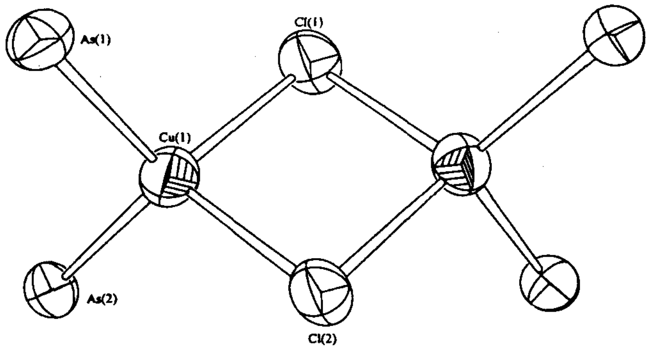

Figure 2. Core structure of $[\{(C_6H_5)_3As\}_2CuCl]_2\cdot 2CDCl_3$ with atom numbering.

Table 4. Comparisons of the selected interatomic distances (Å) and angles (deg) for $[\{(C_6H_5)_3As\}_2CuCl]_2\cdot 2CDCl_3$ (1) and $[\{(C_6H_5)(CH_3)_2As\}_2CuCl]_2\cdot C_6H_6$ (2)

	$1\cdot 2CDCl_3$ This work.	$2\cdot C_6H_6$ Reference [2].
Cu(1)-As(1)	2.391 (2)	2.350 (2)
Cu(1)-As(2)	2.376 (2)	2.367 (2)
Cu(1)-Cl(1)	2.373 (4)	2.374 (4)
Cu(1)-Cl(2)	2.369 (4)	2.385 (4)
As(1)-C(1)	1.923 (13)	1.97 (2)
As(1)-C(7)	1.955 (12)	1.97 (2)
As(1)-C(13)	1.931 (11)	1.94 (1)
As(2)-C(19)	1.948 (11)	1.97 (2)
As(2)-C(25)	1.949 (13)	1.97 (2)
As(2)-C(31)	1.946 (12)	1.94 (1)
Cu(1)···Cu(1)'	3.113 (4)	3.029 (4)
Cl(1)···Cl(2)	3.578 (6)	3.671 (7)
C-C (Ph, avg.)	1.37 (2)	1.39 (2)
As(1)-Cu(1)-As(2)	114.18 (7)	118.00 (9)
As(1)-Cu(1)-Cl(1)	107.42 (7)	105.3 (1)
As(1)-Cu(1)-Cl(2)	107.42 (7)	115.8 (1)
As(1)-Cu(1)-Cu(1)'	117.16 (7)	123.4 (1)
As(2)-Cu(1)-Cl(1)	114.23 (8)	115.1 (1)
As(2)-Cu(1)-Cl(2)	114.21 (8)	100.7 (1)
As(2)-Cu(1)-Cu(1)'	128.67 (8)	118.6 (1)
Cl(1)-Cu(1)-Cl(2)	97.96 (11)	100.9 (1)
Cu(1)-Cl(1)-Cu(1)'	82.0 (2)	79.1 (1)
Cu(1)-As(1)-C(1)	116.0 (4)	113.7 (6)
Cu(1)-As(1)-C(7)	113.9 (4)	118.2 (6)
Cu(1)-As(1)-C(13)	99.3 (5)	118.2 (4)
Cu(1)-As(2)-C(19)	113.8 (3)	114.8 (5)
Cu(1)-As(2)-C(25)	119.9 (4)	117.0 (6)
Cu(1)-As(2)-C(31)	116.7 (4)	120.0 (5)
C(1)-As(1)-C(7)	104.4 (5)	101 (1)
C(1)-As(1)-C(13)	99.3 (5)	100.7 (7)
C(7)-As(1)-C(13)	99.9 (5)	102.2 (7)
C(19)-As(2)-C(25)	101.0 (5)	100.5 (8)
C(19)-As(2)-C(31)	100.1 (5)	100.9 (7)
C(25)-As(2)-C(31)	102.4 (5)	100.6 (7)

9(4)°. Thus, the C(1)-As(1)-C(13) and C(7)-As(1)-C(13) angles are compressed, to be 99.3(5)° and 99.9(5)°, respectively. Other C(ipso)-As-C(ipso) angles are also compressed, ranging from 100.1(5)° to 104.4(5)°.

To the best of our knowledge, the only one previous example of dinuclear copper (I) complex bridged by halogen atoms with four same terminal arsenic ligands fully characterized by X-ray study is $[\{(C_6H_5)(CH_3)_2As\}_2CuCl]_2$ (**2**).[2] Although it has the same geometry of Cu_2Cl_2 rhomboid and the necessary axial arrangements of four terminal arsenic ligands relative to the rhomboid, their interatomic distances and angles are strongly influenced by the characteristics of the bridging halogen atoms and terminal arsenic ligands as summarized in Table 4. The steric size of two arsenic ligands increases in the order of $(C_6H_5)(CH_3)_2As<(C_6H_5)_3As$. Resultant copper (I)-arsenic distances 2.376(2) and 2.391(2) Å of complex **1** are much longer than those of complex **2** [2.350(2) Å], and furthermore, longer than 2.361 Å for tetrameric $[(Et_3As)CuI]_4$.[7] However, the values of 2.376(2) Å and 2.391(2) Å for complex **1** are within the sum of the relevant van der Waals radii of typical copper (*Td*) and arsenic (*Td*) atom (1.35 Å+1.18 Å=2.53 Å).[14] The lengthening of the copper (I)-arsenic bonds also reflects the relative weakness of the bonds and affects the bond strength of the copper-chlorine bonds. Copper (I)-chlorine bond lengths of complex **1** [2.369(4) and 2.373(4) Å] are slightly shorter than those of complex **2** [2.374(4) and 2.385(4) Å].

In Figure 2, the d^{10} copper (I) atom has a highly distorted tetrahedral geometry. The As(1)-Cu(1)-As(2) angle of 114.18(7)°, compared with 97.96(11)° for the Cl(1)-Cu(1)-Cl(2) angle, also shows the greater bulk of the triphenylarsine ligands compared with the chlorine ligands.

Previously it was predicted by Teo and Calabrese[10] that for $[\{(C_6H_5)_3As\}CuX]_4$ series (X=Cl; Br; I) the tetrameric cubane → chair isomerism or transformation would take place between the $[\{(C_6H_5)_3P\}AgX]_4$ and the $[\{(C_6H_5)_3As\}CuX]_4$ series, especially in the vicinity of $[\{(C_6H_5)_3As\}CuBr]_4$. However, the structure of the $[\{(C_6H_5)_3As\}CuI]_4$ has been proved to be cubane-like form by Churchill and Youngs[8] and $[\{(C_6H_5)_3As\}CuCl]_4$ has not been isolated yet. It is noteworthy that the $[\{(C_6H_5)_3As\}_2CuCl]_2$ structure does exist as a dimeric form rather than tetrameric one like $[\{(C_6H_5)_3As\}CuI]_4$ and $[\{(C_6H_5)_3P\}CuCl]_4$.[7,15] But at this stage we cannot rule out possible formation of homologous tetrameric $[\{(C_6H_5)_3As\}CuCl]_4$.

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