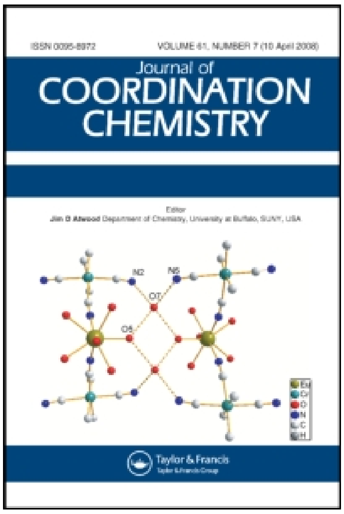

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Steric control of tritolylphosphines on the nuclearity of Cu(I) complexes: Syntheses and structures of the iodo-bridged $[Cu_4(\mu_3\text{-}I)_4(p\text{-tolyl}_3P)_4]$ cubane and the $[Cu_2(\mu\text{-}I)_2(o\text{-tolyl}_3P)_2]$ dimer

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The preparation and crystal structures of copper(I) iodide complexes with tri-*o*-tolylphosphine (o-tolyl$_3$P) and tri-*p*-tolylphosphine (p-tolyl$_3$P) are described. While p-tolyl$_3$P forms an iodo-bridged cubane, $[Cu_4I_4(p\text{-tolyl}_3P)_4]$, **1**, o-tolyl$_3$P forms a dimer, $[Cu_2I_2(o\text{-tolyl}_3P)_2]$, **2**. In **1**, each Cu is bonded to one P atom of p-tolyl$_3$P {Cu–P, 2.248(2), 2.243(5) Å} and three iodide ligands {Cu–I, 2.690(1), 2.686(2), 2.663(2) Å}. I–Cu–I bond angles are in the range 67–70° and Cu–I–Cu vary between 106 and 112°. In **2**, the central unit, $Cu(\mu\text{-}I)_2Cu$, forms a parallelogram with unequal Cu–I distances {Cu–I, 2.601(1), 2.579(1) Å} and bond angles {Cu–I–Cu, 74.42(3), I–Cu–I, 105.58(3)°}. Each Cu atom is further bonded to one P atom of o-tolyl$_3$P {Cu–P, 2.246(2) Å}.

Keywords: Copper(I); Tri-tolylphosphines; Iodide; Bridging; X-ray structure

1. Introduction

Tertiary phosphines (PR_3) react with copper(I) halides to form tetranuclear complexes of stoichiometry $[(PR_3)CuX]_4$, {$PR_3 = PPh_3$, X = Cl (**4**), Br (**5**), I (**6**); $PR_3 = PEt_3$, X = Cl (**7**), Br (**8**), I (**9**); $PR_3 = PMePh_2$, X = I (**10**), $PR_3 = t\text{-}Bu_3P$, X = Br (**11**)} and $[(PPh_3)CuBr]_4 \cdot 2CHCl_3$ **12** [1–9]. Compounds **4**, **7**–**11** have a cubane structure, while **5**, **6** and **12** have step-like structure. However, for compounds **5** and **6**, cubane isomers are also known [10]. Tertiary phosphines (PR_3) also form limited three coordinate symmetrical dimers, $[Cu_2(\mu\text{-}I)_2(PCy_3)_2]$, **13**, $[Cu_2(\mu\text{-}I)_2(o\text{-tolyl}_3P)_2] \cdot PhCH_3$, **14**, and

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$[Cu_2(\mu\text{-}I)_2L_2]$ {L = PPh(mesityl)$_2$, **15**, PPh$_2$(mesityl), **16**} [11–13]. In contrast, there are several symmetrical dimers involving tetracoordination at each Cu centre [11–19].

In continuation of previous work on the formation of dinuclear, trinuclear and polymeric networks with transition metals [20,21], it was decided to observe the effect of the position of the methyl group in the phenyl ring attached to P and thus carry out reactions of tri-tolylphosphines with copper(I) iodide. The construction of unusual metal clusters and multidirectional networks containing copper(I) and silver(I) is of some interest, as some of them display conducting properties [22]. Reaction of copper(I) iodide with tri-*m*-tolylphosphine in acetonitrile yields an unprecedented bicapped adamantoid complex $[Cu_6(\mu_2\text{-}I)(\mu_3\text{-}I)_4(\mu_4\text{-}I)(m\text{-tolyl}_3P)_4(CH_3CN)_2]$ cluster, **3** [23]. In this article, a dimer and a cubane formed by reaction of copper(I) iodide with tri-*o*-tolylphosphine and tri-*p*-tolylphosphine, respectively, are described.

2. Experimental

2.1. *Materials and techniques*

Copper(I) iodide was prepared by reducing an aqueous solution of $CuSO_4 \cdot 5H_2O$ with SO_2 in the presence of a stoichiometric amount of sodium iodide in water [24]. The ligands tri-*o*-tolylphosphine (*o*-tolyl$_3$P) and tri-*p*-tolylphosphine (*p*-tolyl$_3$P) were purchased from Sigma-Aldrich Ltd. Elemental analyses for C, H and N were carried out with a Carlo-Erba 1108 instrument.

2.2. *Syntheses of the complexes*

2.2.1. Complex 1. To a stirred solution of copper(I) iodide (0.043 g, 0.22 mmol) in acetonitrile (10 cm^3) was added a solution of tri-*p*-tolylphosphine (0.068 g, 0.22 mmol) in chloroform (10 cm^3) and the mixture stirred for 4 h. The resulting clear yellow solution was allowed to crystallize and a light yellow compound formed. Yield, 65%; m.p. 250–260°C. Satisfactory analytical data were obtained. Crystals were grown from an acetonitrile–chloroform mixture.

2.2.2. Complex 2. To a stirred solution of copper(I) iodide (0.037 g, 0.19 mmol) in acetonitrile (10 cm^3) was added a solution of tri-*o*-tolylphosphine (0.059 g, 0.19 mmol) in methanol (10 cm^3) and the mixture stirred for 2 h. Slow evaporation of the resulting solution gave colourless crystals. Yield: 55%; m.p. 240–245°C. Satisfactory analytical data were obtained. Crystals were grown from an acetonitrile–methanol mixture.

2.3. *X-ray crystallography*

A yellow prismatic crystal of **1** was mounted on a glass fibre and used for data collection. Intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 193 K. Data were processed using the Crystal Clear program (Rigaku). A symmetry-related absorption correction using the program REQAB was applied and data were corrected for Lorentz and polarization effects. All calculations were performed using SGI INDY.

Table 1. Crystal data and refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{84}H_{84}Cu_4I_4P_4$	$C_{42}H_{42}Cu_2I_2P_2$
M	1979.28	989.58
Temperatue (K)	193(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	trigonal	triclinic
Space group	$R\bar{3}$	$P\bar{1}$
a (Å)	16.655(3)	9.361(3)
b (Å)	16.655(3)	10.121(3)
c (Å)	52.82(1)	11.683(3)
α (°)		102.164(6)
β (°)		99.059(6)
γ (°)		101.798(6)
V (Å³)	12688(4)	1035.6(5)
Z	6	1
D_{calc} (Mg m^{-3})	1.554	1.587
μ (Mo K_α) (mm^{-1})	2.568	2.621
Reflections collected	41468	6018
Independent reflections	6415 ($R_{int} = 0.135$)	4208 ($R_{int} = 0.0315$)
R indices [$I > 2\sigma(I)$]		
R	0.053	0.0603
*WR*2 (all data)	0.146	0.1235

The structure was solved by direct methods using the program SIR 92 and refined by full-matrix least-squares techniques against F^2 using the SHELXL-97 and teXsan program as part of a graphical interface [25–27]. Non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically; the remainder were included in fixed positions.

A colourless prismatic crystal of **2** was mounted on a glass fibre and used for data collection. Crystal data were collected at 293(2) K using a Bruker SMART CCD 1000 diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used throughout. Data were processed with SAINT [28] and corrected for absorption using SADABS [29]. The structure was solved by direct methods using SHELXS [30], and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [31]. Positional and anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were positioned geometrically, and positional parameters were refined using a riding model. Crystallographic data are summarized in table 1.

3. Results and discussion

Reactions of copper(I) iodide with tri-*p*-tolylphosphine or tri-*o*-tolylphosphine in 1 : 1 molar ratio in acetonitrile formed complexes of stoichiometry {CuI(*p*-tolyl$_3$P)} and {CuI(*o*-tolyl$_3$P)}. Crystal structure determinations have shown the former to possess a cubane structure, [Cu_4I_4(*p*-tolyl$_3$P)$_4$], **1**, and the latter a dimeric structure, [Cu_2I_2(*o*-tolyl$_3$P)$_2$], **2**. Interestingly, reaction of *m*-tolyl$_3$P with copper(I) iodide formed an unprecedented bicapped adamantoid structure, [Cu_6(μ_2-I)(μ_3-I)$_4$(μ_4-I)(*m*-tolyl$_3$P)$_4$(CH_3CN)$_2$], **3** [23].

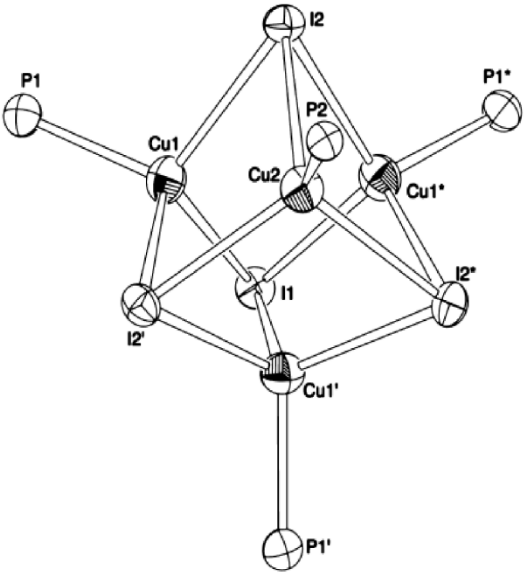

Figure 1. Structure of compound **1** with the atom numbering scheme (*p*-tolyl groups are omitted for clarity).

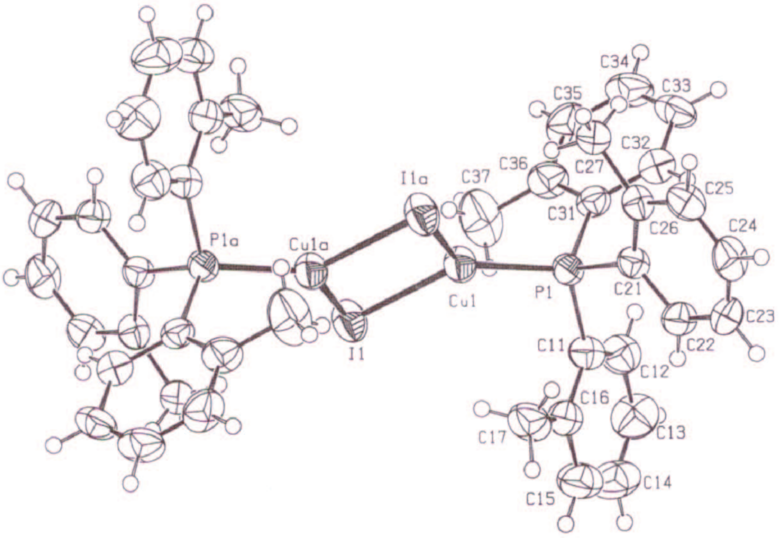

Figure 2. Structure of compound **2** with the atom numbering scheme.

3.1. *Crystal structures of 1 and 2*

Figures 1 and 2 show the molecular structures of cubane **1** and dimer **2**, respectively, along with their atom numbering schemes. In **1**, each Cu is bonded to one P and three I atoms. All four I atoms are triply bridging. I(1) is bonded to three Cu atoms {Cu(1), Cu(1)*, Cu(1)′} at 2.690(1) Å, while I(2) is bonded to Cu(1)*, Cu(2) atoms at 2.686(2) Å and to Cu(1) at a somewhat shorter distance, 2.663(2) Å (table 2). All Cu–I distances are much less than the sum of the ionic radii of Cu^+ and I^-, 2.97 Å [32].

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
I(1)–Cu(1)	$2.690(1)^{\#1}$	I(2)–Cu(1)	$2.663(2)^{\#2}$
I(1)–Cu(1)*	$2.690(1)^{\#2}$	I(2)–Cu(2)	$2.686(1)^{\#1}$
I(1)–Cu(1)′	$2.690(1)^{\#3}$	Cu(1)–P(1)	$2.248(2)^{\#1}$
I(2)–Cu(1)*	$2.686(2)^{\#1}$	Cu(2)–P(2)	$2.243(5)^{\#1}$
Cu(1)–I(1)–Cu(1)*	67.14(4)	I(1)–Cu(1)–P(1)	111.52(8)
Cu(1)–I(2)–Cu(1)*	67.59(5)	I(2)–Cu(1)–I(2)′	106.93(5)
Cu(1)–I(2)–Cu(2)	69.75(5)	I(2)–Cu(1)–P(1)	110.4(1)
Cu(1)–I(2)′–Cu(2)	70.09(5)	I(2)′–Cu(1)–P(1)	110.1(1)
I(1)–Cu(1)–I(2)	108.52(6)	I(2)–Cu(2)–I(2)′	106.30(5)
I(1)–Cu(1)–I(2)′	109.20(5)	I(2)–Cu(2)–P(2)	112.48(4)
2			
Cu(1)–P(1)	2.2460(18)	P(1)–C(31)	1.839(6)
I(1)–Cu(1)	2.6014(11)	P(1)–C(11)	1.838(6)
$I(1)^{\#4}$–Cu(1)	2.5794(11)	$Cu(1)–Cu(1)^{\#4}$	3.1332(17)
$I(1)–Cu(1)^{\#4}$	2.5794(11)	$I(1)–I(1)^{\#4}$	4.1261(12)
P(1)–C(21)	1.825(6)		
$P(1)–Cu(1)–I(1)^{\#4}$	127.61(6)	$I(1)^{\#4}$–Cu(1)–I(1)	105.58(3)
P(1)–Cu(1)–I(1)	126.47(6)	$Cu(1)–I(1)–Cu(1)^{\#4}$	74.42(3)

Symmetry transformations used to generate equivalent atoms are: #1: *x*, *y*, *z*; #2: −*y*, *x*−*y*, *z*; #3: −*x*+*y*, −*x*, *z*; #4: 1−*x*, 1−*y*, 1−*z*.

Table 3. A comparison of bond lengths (Å) and angles (°) in various Cu(I) cubanes and dimers.

	Cubanes					
	Cu–P	Cu–I	Cu–I–Cu	I–Cu–I	P–Cu–I	Ref.
1	2.246	2.676	68.64	107.7	110.7	This work
6	2.254	2.692	69.76	109.0	111.7	[10]
9	2.254	2.684	66.10	109.4	109.6	[5]
10	2.250	2.689	67.75	109.5	109.2	[6]
		Cu–I/Cu–I′	Dimers		P–Cu–I/P–Cu–I′	
2	2.246	2.601, 2.579	74.42	105.6	127.6, 126.5	This work
13	2.225	2.562, 2.578	68.50	111.5		[11]
14	2.238	2.640, 2.525	74.30	105.7	136.6, 117.7	[12]
15	2.201	2.589, 2.554	63.5	116.0		[13]
16	2.222	2.553, 2.569	63.7	114.9		[13]

Cu–P bond distances are equal {Cu(1)–P(1), 2.248(2) Å and Cu(2)–P(2), 2.243(5) Å}. I–Cu–I angles at Cu centres are in the range 106–109°, while those at I atoms are 67–70°. There is no Cu$\cdots$Cu contact less than 2.80 Å [32]. Table 3 shows a comparison of some bond parameters with other cubanes of copper(I) iodide reported in the literature. It can be seen that various parameters of **1** are similar to those listed for other related species.

In the dimer, **2**, Cu–I bond distances of 2.5794(11) and 2.6014(11) Å show that the central Cu(μ-I)$_2$Cu group forms a parallelogram. As expected, these bonds are stronger than those observed in **1**. However, the Cu(1)–P(1) bond distance of 2.2460(18) Å, is similar to that shown in **1**. The Cu$\cdots$Cu distance of 3.13 Å gives no evidence for any metal–metal interaction. Angles within the Cu(μ-I)$_2$Cu core, Cu(1)–I(1)–Cu(1) and I(1)–Cu(1) –I(1), are 74.42(3) and 105.58(3)°, respectively. Compound **2** is triclinic, whereas the dimer **14** is monoclinic [12]. The difference may be attributed to different solvents used in the two cases, acetonitrile–toluene for **14** and acetonitrile–methanol for **2**.

It is seen from table 3 that various bonding parameters for **2** are similar to those of the other dimers listed. The most significant variation between **2** and **14** lies in the fact that P–Cu–I/P–Cu–I′ bond angles are entirely different. This must be the consequence of the different crystal modifications.

Supplementary material

Full lists of crystallographic data have been deposited with the CCDC with deposition numbers CCDC 229704 for **1** and CCDC 229705 for **2**.

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