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Two New Modifications of $[P(C_6H_5)_4]_2[Cu_2I_4]$

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Abstract. Single crystals of two new modifications of $[P(C_6H_5)_4]_2[Cu_2I_4]$ were obtained by reaction of granulated copper with iodine and $[P(C_6H_5)_4]I$ in dry acetone under nitrogen atmosphere. They crystallise monoclinically, space group $P2_1/n$ (No. 14), $a = 11.550(6)$, $b = 7.236(2)$, $c = 27.232(13)$ Å, $\beta = 98.13(3)°$, $V = 2253(2)$ Å^3, and $Z = 2$ ($[P(C_6H_5)_4]_2[Cu_2I_4]$-C), and space group Cc (No. 9), $a = 17.133(5)$, $b = 15.941(5)$, $c = 18.762$ (6) Å, $\beta = 114.02(1)°$, $V = 4681(3)$ Å^3, and $Z = 4$ ($[P(C_6H_5)_4]_2[Cu_2I_4]$-D), respectively. In these compounds the $[CuI_2]^-$ anions form dimers di-μ-iodo-diiodocuprate(I), which are either planar (**C**) or folded (**D**).

Keywords: Iodocuprate(I); $[Cu_2I_4]^{2-}$; tetraphenylphosphonium; crystal structure

Zwei neue Modifikationen von $[P(C_6H_5)_4]_2[Cu_2I_4]$

Inhaltsübersicht. Bei der Reaktion von granuliertem Kupfer mit Iod und $[P(C_6H_5)_4]I$ in trockenem Aceton unter Stickstoffatmosphäre wurden Einkristalle von zwei neuen Modifikationen von $[P(C_6H_5)_4]_2[Cu_2I_4]$ erhalten. Sie kristallisieren monoklin, Raumgruppe $P2_1/n$ (Nr. 14), $a = 11.550(6)$, $b = 7.236$ (2), $c = 27.232$ (13) Å, $\beta = 98.13(3)°$, $V = 2253(2)$ Å^3 und $Z = 2$ ($[P(C_6H_5)_4]_2[Cu_2I_4]$-C) bzw. Raumgruppe Cc (Nr. 9), $a = 17.133(5)$, $b = 15.941(5)$, $c = 18.762(6)$ Å, $\beta = 114.02(1)°$, $V = 4681(3)$ Å^3 und $Z = 4$ ($[P(C_6H_5)_4]_2[Cu_2I_4]$-D). In diesen Verbindungen liegen dimere di-μ-iodo-diiodocuprat(I)-Einheiten vor, die planar (**C**) bzw. gewinkelt (**D**) sind.

1 Introduction

Only a few compounds containing dimeric anions $[Cu_2I_4]^{2-}$ are reported in the literature. A recent review on halogenocuprates(I) [1] reports that $[Cu_2I_4]^{2-}$ units crystallising with large $[NR_4]^+$, $[PR_4]^+$ or $[AsR_4]^+$ cations (R = alkyl or phenyl) are either planar or folded. For R = phenyl two modifications have been described by *Hartl* et al. [2a], one of them containing the planar ($[PPh_4]_2[Cu_2I_4]$-A) (Ph = C_6H_5) and the second one the folded ($[PPh_4]_2[Cu_2I_4]$-B) form of the dianion, comparable to those shown in Fig. 1. According to refs. [2a, 2b, 3] the experimental condi-

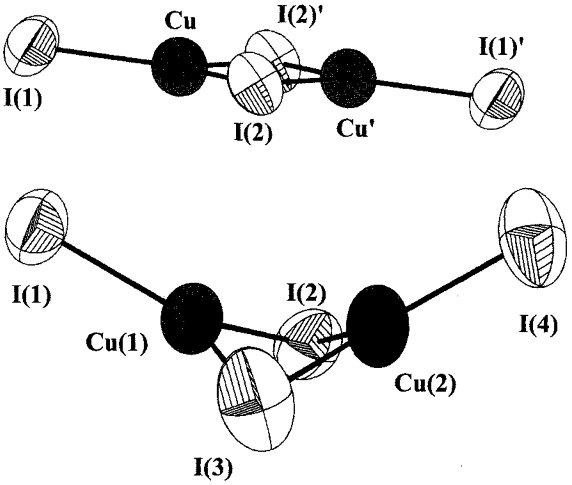

Fig. 1 Arrangement of atoms and labelling scheme for the two geometrically different $[Cu_2I_4]^{2-}$ dianions as observed in a) $[PPh_4]_2[Cu_2I_4]$-C (atoms related by the centre of symmetry are marked by ′), and b) $[PPh_4]_2[Cu_2I_4]$-D. Ellipsoids represent a probability of 75%.

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tions and the kind of the counterion strongly influence the geometry of the $[Cu_2I_4]^{2-}$ ion. This would suggest that the $[Cu_2I_4]^{2-}$ unit shows some strong interactions with the surrounding $[PPh]^+$ cations and fits their different way of packing. Thus the planar and the folded form of the $[Cu_2I_4]^{2-}$ dianion might be regarded as two examples of the same anion. It is well known that copper(I) halides are very flexible and can adapt the necessities of different bonding partners. Systematic studies have been performed e. g. on compounds of copper(I) halides with neutral polymers of group 15 and 16 elements (e. g. CuXSeTe, CuXSTe, $(CuI)_3P_{12}$, $(CuI)_2P_{14}$ [4–7]) or respective compounds containing thiometalate anions (e. g. $(CuI)_3Cu_2TeS_3$ [8]). Nevertheless the existence of two different modifications of e. g. $[AsPh_4]Br_3$ [9, 10] containing an almost unchanged Br_3^- ion shows that the hitherto known modifications of $[PPh_4]_2[Cu_2I_4]$ could also be regarded as examples of two different compounds. That means the planar and the folded $[Cu_2I_4]^{2-}$ unit might be described as different dianions. Here we report on synthesis and structural characterisation of two new modifications of $[PPh_4]_2[Cu_2I_4]$ namely **C** and **D**, representing a respective alternative stacking version for both different dianions with $[PPh_4]^+$.

2 X-ray Structure Determination

The crystal structures of the title compounds were solved by direct methods (NRCVAX, [11]) and refined against F^2 by the SHELXL-93 program [12], for details see Table 1. For $[PPh_4]_2[Cu_2I_4]$-D no solution was found assuming a centrosymmetric space group. From the structure solution the positional parameters of iodine, copper, phosphorus and some carbon atoms were obtained. H atoms were determined by difference Fourier calculations for $[PPh_4]_2[Cu_2I_4]$-C, and introduced at their best positions for $[PPh_4]_2[Cu_2I_4]$-D, respectively. During the refinement a fixed $U_{iso}(H) = 0.05$ Å^2 was used for both compounds. For **D** three of 48 carbon atoms were refined in a split model (isotropic displacement parameters for the split atoms). Table 2 contains the positional parameters and equivalent atomic displacement parameters for $[PPh_4]_2[Cu_2I_4]$-C, the corresponding values for

Table 1 Crystallographic data (e. s. d.'s) for the structure analyses of $[PPh_4]_2[Cu_2I_4]$-C and $[PPh_4]_2[Cu_2I_4]$-D

Compound	$[PPh_4]_2[Cu_2I_4]$-C	$[PPh_4]_2[Cu_2I_4]$-D
Formula weight (g mol^{-1})	– 1313.42 –	
Crystal size (mm^3)	0.15 × 0.38 × 0.90	0.12 × 0.16 × 0.36
Cell setting	– monoclinic –	
Space group	$P2_1/n$ (No. 14)	Cc (No. 9)
Lattice constants (Å)	$a = 11.550(6)$	$a = 17.133(5)$
from single crystals	$b = 7.236(2)$	$b = 15.941(5)$
	$c = 27.232(13)$	$c = 18.762(6)$
	$\beta = 98.13(3)°$	$\beta = 114.02(1)$
Cell volume (Å^3), Z	2253(2), 2	4681(3), 4
$\rho_{x\text{-ray}}$ (g cm^{-3})	1.936	1.864
Diffractometer	NONIUS CAD4, MoKα, oriented graphite monochromator	
Scan type	– ω-scans –	
Temperature	298 K	298 K
2θ-range (°)	$2 < 2\theta < 50$	$2 < 2\theta < 60$
hkl-range	$-13 \le h \le 0$	$-24 \le h \le 20$
	$-8 \le k \le 0$	$0 \le k \le 22$
	$-32 \le l \le 32$	$-24 \le l \le 26$
No. of reflections, $R_{int.}$	4175, 0.0282	10524, 0.0375
No. of independent reflections	3962	10238
No. of parameters	313	503
$R1$ [a]) ($I > 2\sigma_I$), $R1$ [a]) (all reflections)	0.0506, 0.1041	0.0759, 0.1923
$wR2$ [a]) ($I > 2\sigma_I$), $wR2$ [a]) (all reflections)	0.1208, 0.1449	0.1733, 0.2289
GooF [a])	1.070	1.025
Weighting parameters [b])	$a = 0.07985$	$a = 0.1167$ $b = 13.3611$
Largest difference peak $\Delta\rho_{max}$	1.132	1.158
and hole $\Delta\rho_{min}$ (eÅ^{-3})	–0.986	–1.339
Flack parameter	–	0.03(5)

[a]) $R1 = \dfrac{\Sigma||F_o| - |F_o||}{\Sigma|F_o|}$, $wR2 = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma[w(F_o^2)^2]}}$, $\text{GooF} = \sqrt{\dfrac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$

[b]) $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$, $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} [a] ($Å^2 \times 10^3$) for $[PPh_4]_2[Cu_2I_4]$-C.

Atom	x	y	z	U_{eq}
I(1)	4532(1)	1047(1)	1382(1)	66(1)
I(2)	4207(1)	2583(1)	–253(1)	55(1)
Cu	4863(1)	464(2)	497(1)	58(1)
P	310(2)	1478(3)	8577(1)	28(1)
C(11)	1149(7)	48(10)	9035(3)	32(2)
C(12)	1073(7)	215(13)	9526(3)	42(2)
C(13)	1735(9)	–963(17)	9862(3)	60(3)
C(14)	2450(8)	–2267(15)	9707(4)	53(3)
C(15)	2522(8)	–2406(12)	9215(4)	50(2)
C(16)	1875(10)	–1284(15)	8875(3)	48(3)
C(21)	1259(7)	2958(10)	8289(3)	32(2)
C(22)	2451(7)	2972(12)	8439(3)	41(2)
C(23)	3130(9)	4261(14)	8232(4)	55(2)
C(24)	2621(10)	5495(13)	7875(4)	59(3)
C(25)	1444(9)	5439(12)	7723(4)	51(2)
C(26)	745(8)	4190(12)	7930(3)	44(2)
C(31)	–495(6)	–37(10)	8136(3)	29(2)
C(32)	–438(7)	40(12)	7633(3)	39(2)
C(33)	–1040(8)	–1259(14)	7316(3)	49(2)
C(34)	–1671(8)	–2591(14)	7500(3)	48(2)
C(35)	–1758(8)	–2684(12)	7999(4)	48(2)
C(36)	–1175(8)	–1412(12)	8311(3)	41(2)
C(41)	–654(7)	2945(10)	8867(3)	32(2)
C(42)	–1845(7)	2663(13)	8815(3)	40(2)
C(43)	–2553(9)	3848(16)	9042(3)	56(3)
C(44)	–2032(11)	5329(14)	9315(4)	61(3)
C(45)	–866(11)	5568(13)	9374(4)	56(3)
C(46)	–137(9)	4423(12)	9148(3)	45(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

$[PPh_4]_2[Cu_2I_4]$-D are summarised in Table 3. Selected interatomic distances and angles are given in Table 4. Typical bond lengths, i.e. d(P–C) ≈ 1.79 Å and d(C–C) ≈ 1.36 Å, are not listed[1]).

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} [a] ($Å^2 \times 10^3$) for $[PPh_4]_2[Cu_2I_4]$-D.

Atom	x	y	z	U_{eq}
I(1)	5357(1)	9918(1)	6406(1)	61(1)
I(2)	5734(1)	7533(1)	5413(1)	53(1)
I(3)	7162(1)	9708(1)	5235(1)	84(1)
I(4)	8603(1)	7405(1)	6470(1)	76(1)
Cu(1)	6069(2)	9113(2)	5724(2)	58(1)
Cu(2)	7273(2)	8175(2)	5720(2)	65(1)
P(1)	7143(3)	5732(3)	8305(2)	37(1)
P(2)	8583(3)	8209(3)	3321(2)	39(1)
C(11)	7151(10)	5274(11)	9188(10)	38(4)
C(12)	7901(12)	5042(11)	9815(10)	44(4)
C(13)	7864(13)	4700(12)	10439(11)	53(5)
C(14)	7078(15)	4567(13)	10503(13)	64(6)
C(15)	6323(15)	4782(12)	9882(12)	56(5)
C(16)	6347(11)	5153(13)	9223(12)	52(5)
C(21)	7018(12)	6867(11)	8338(10)	40(4)
C(22)	7146(13)	7360(11)	7798(11)	47(5)
C(23)	7002(12)	8197(14)	7755(12)	57(6)
C(24)	6741(13)	8560(12)	8295(12)	55(5)
C(25)	6634(14)	8084(15)	8849(13)	63(6)
C(26)	6771(11)	7236(11)	8895(11)	40(4)
C(31)	6265(11)	5313(12)	7512(10)	43(5)
C(32)	5718(12)	5813(12)	6912(10)	46(4)
C(33)	5015(13)	5430(14)	6299(14)	60(6)
C(34)	4892(15)	4618(17)	6329(14)	73(7)
C(35)	5437(13)	4051(15)	6884(12)	62(6)
C(36)	6123(12)	4449(13)	7467(12)	50(5)
C(41)	8151(10)	5512(12)	8235(10)	40(4)
C(42)	8840(12)	5950(13)	8709(11)	51(5)
C(43)	9627(11)	5791(13)	8662(13)	56(6)
C(44)	9684(14)	5225(15)	8116(14)	65(6)
C(45)	8943(13)	4830(12)	7615(13)	52(5)
C(46)	8153(12)	4983(12)	7662(11)	45(5)
C(51)	8637(12)	7818(15)	2462(11)	61(6)
C(52)	9363(13)	7579(13)	2426(11)	54(5)
C(53)	9436(15)	7288(13)	1761(12)	57(6)
C(54 A)	8793(31)	7409(39)	1102(31)	44(12)
C(55 A)	8044(44)	7802(42)	1007(42)	80(20)
C(56 A)	7978(38)	8087(41)	1742(33)	68(18)
C(54 B)	8744(25)	6989(31)	1161(25)	66(11)
C(55 B)	7970(29)	7071(27)	1222(26)	81(13)
C(56 B)	7905(21)	7428(22)	1836(19)	53(9)
C(61)	9446(11)	7715(11)	4138(10)	39(4)
C(62)	9995(11)	8168(12)	4729(10)	46(4)
C(63)	10619(14)	7708(17)	5370(13)	73(7)
C(64)	10669(13)	6888(14)	5402(14)	57(5)
C(65)	10094(13)	6436(13)	4756(12)	54(5)
C(66)	9475(11)	6850(13)	4150(11)	47(5)
C(71)	7583(11)	7949(12)	3369(10)	40(4)
C(72)	7527(14)	7441(13)	3920(12)	54(5)
C(73)	6767(16)	7258(15)	3951(15)	65(6)
C(74)	6030(16)	7600(14)	3405(17)	70(7)
C(75)	6040(16)	8123(18)	2845(16)	84(8)
C(76)	6845(12)	8354(13)	2822(12)	55(5)
C(81)	8711(12)	9310(13)	3372(12)	55(5)
C(82)	8621(15)	9763(13)	3985(12)	59(6)
C(83)	8714(13)	10583(14)	4046(14)	69(7)
C(84)	8964(14)	11008(16)	3506(18)	77(8)
C(85)	9051(21)	10584(21)	2898(23)	128(15)
C(86)	8934(15)	9783(16)	2840(15)	69(7)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

3 Description and Discussion of the Crystal Structures

$[PPh_4]_2[Cu_2I_4]$-C

The copper atoms in both new modifications of $[PPh_4]_2[Cu_2I_4]$ are threefold coordinated by iodine and the resulting $[CuI I_{2/2}]$-units are linked by two bridging iodine atoms. Thus dimeric $[Cu_2I_4]^{2-}$ anions are built. In $[PPh_4]_2[Cu_2I_4]$-C the dianion has a centre of symmetry and the iodine atoms are arranged in a

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[1]) Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406921 ($[P(C_6H_5)_4]_2[Cu_2I_4]$-C), and CSD-406922 ($[P(C_6H_5)_4]_2[Cu_2I_4]$-D), respectively.

Table 4 Selected interatomic distances (Å) and angles (°) for the $[Cu_2I_4]^{2-}$ units as observed in $[PPh_4]_2[Cu_2I_4]$-C and $[PPh_4]_2[Cu_2I_4]$-D. Iodine atoms are marked as terminal (^{t}), and bridging (^{b}), respectively.

$[PPh_4]_2[Cu_2I_4]$-C			
Cu–I(1)^t	2.527(2)	I(1)–Cu–I(2)	120.82(5)
Cu–I(2)^b	2.580(2)	I(1)–Cu–I(2′)	126.04(6)
Cu–I(2′)^b	2.581(2)	I(2)–Cu–I(2′)	112.97(5)
Cu–Cu′	2.849(3)	Cu–I(2)–Cu′	67.03(5)
$[PPh_4]_2[Cu_2I_4]$-D			
Cu(1)–I(1)^t	2.459(3)	I(1)–Cu(1)–I(2)	120.78(11)
Cu(1)–I(2)^b	2.596(3)	I(1)–Cu(1)–I(3)	125.39(12)
Cu(1)–I(3)^b	2.578(3)	I(2)–Cu(1)–I(3)	113.82(10)
Cu(2)–I(2)^b	2.664(3)	I(2)–Cu(2)–I(3)	111.24(10)
Cu(2)–I(3)^b	2.589(3)	I(2)–Cu(2)–I(4)	122.42(12)
Cu(2)–I(4)^t	2.463(3)	I(3)–Cu(2)–I(4)	126.15(12)
Cu(1)–Cu(2)	2.550(3)	Cu(1)–I(2)–Cu(2)	57.98(8)
		Cu(1)–I(3)–Cu(2)	59.14(8)

plane, see Fig. 1. The copper atoms are shifted 0.060(1) Å out of the plane of the surrounding iodine atoms. A distance d(Cu–Cu′) = 2.849(3) Å results, which is slightly longer than the shortest possible distance for the given coordination. As reported by *Jagner* and *Helgesson* [1] the distance d(Cu–Cu) varies in a range from ca. 2.7 Å to 3.0 Å within these planar $[Cu_2I_4]^{2-}$ dianions. The distances d(Cu–I) follow the trend known from further examples, i. e. they are shorter for terminal iodine atoms (d(Cu–I^t) = 2.527 Å) than those for bridging atoms ($\bar{d}$(Cu–I^b) = 2.58 Å).

In Fig. 2 a section of the crystal structure of $[PPh_4]_2[Cu_2I_4]$-C is plotted. Obviously the way of packing the ions is very effective and a calculated density of $\rho_{x\text{-ray}} = 1.936$ g cm^{-3}, which is significantly higher than for the three other modifications of $[PPh_4]_2[Cu_2I_4]$, is obtained. A more detailed description is given below.

$[PPh_4]_2[Cu_2I_4]$-D

In contrast to the planar dimeric $[Cu_2I_4]^{2-}$ unit observed in $[PPh_4]_2[Cu_2I_4]$-C, a further example for a folded dianion is found in $[PPh_4]_2[Cu_2I_4]$-D, see Fig. 1. Again the copper atoms are slightly shifted out of the plane of the three surrounding iodine atoms for 0.013(3) Å (Cu(1)) and 0.065(3) Å (Cu(2)). However, since the angle described by the two iodine planes (i. e. I(1)–I(2)–(I3) and I(2)–I(3)–I(4)) is only 121.44(4)°, the copper atoms are in a relatively close contact, i. e. d(Cu(1)–Cu(2)) = 2.550(3) Å. This distance is ca. 0.1 Å shorter than that found in comparable $[Cu_2I_4]^{2-}$ dianions [1, 2]. The distance $\bar{d}$(Cu–I^t) = 2.46 Å for the folded dianion is shorter than for the planar one. For the bridging iodine atoms they vary in the range $2.57 < d(\text{Cu–I}^b) < 2.67$ Å. The three-dimensional arrangement of the $[PPh_4]^+$ and $[Cu_2I_4]^{2-}$ ions is shown in Fig. 3.

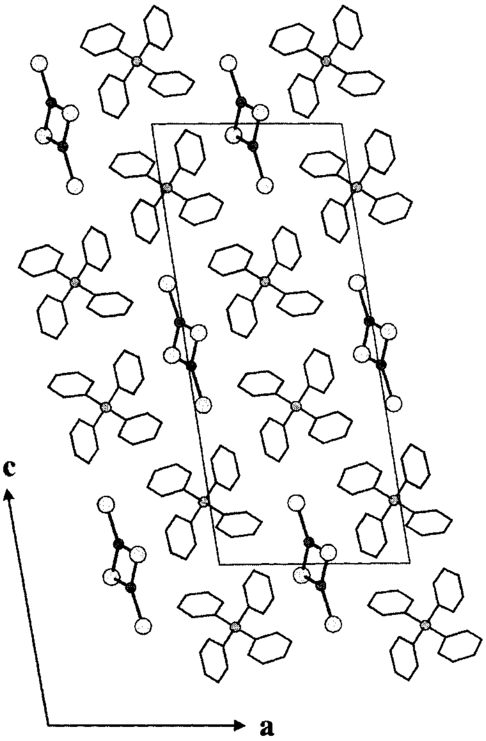

Fig. 2 Section of the crystal structure of $[PPh_4]_2[Cu_2I_4]$-C. Hydrogen atoms are omitted for clarity.

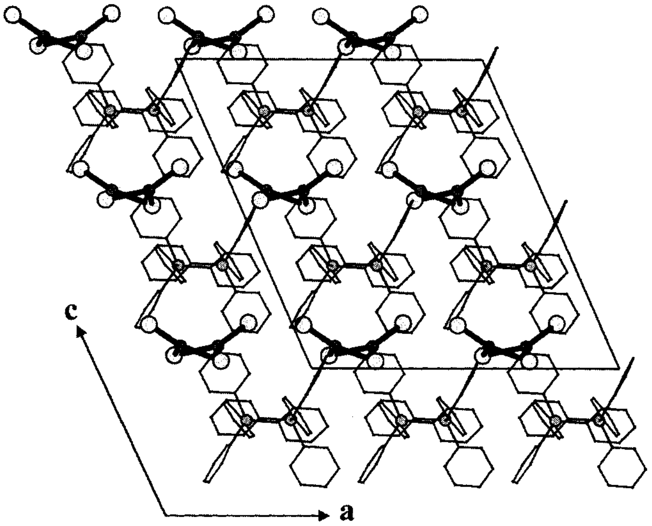

Fig. 3 Section of the crystal structure of $[PPh_4]_2[Cu_2I_4]$-D. Hydrogen atoms are omitted for clarity.

Comparison of the four known modifications of $[PPh_4]_2[Cu_2I_4]$

A crystallographic discussion of group-subgroup relationships for tetraphenylphosphonium and -arsonium salts of monovalent anions was given by *Müller* [13]. He found a stacking of the cations along a $\bar{4}$ axis (in an ideal case) to be often observed in those compounds. According to ref. [13] a major condition for

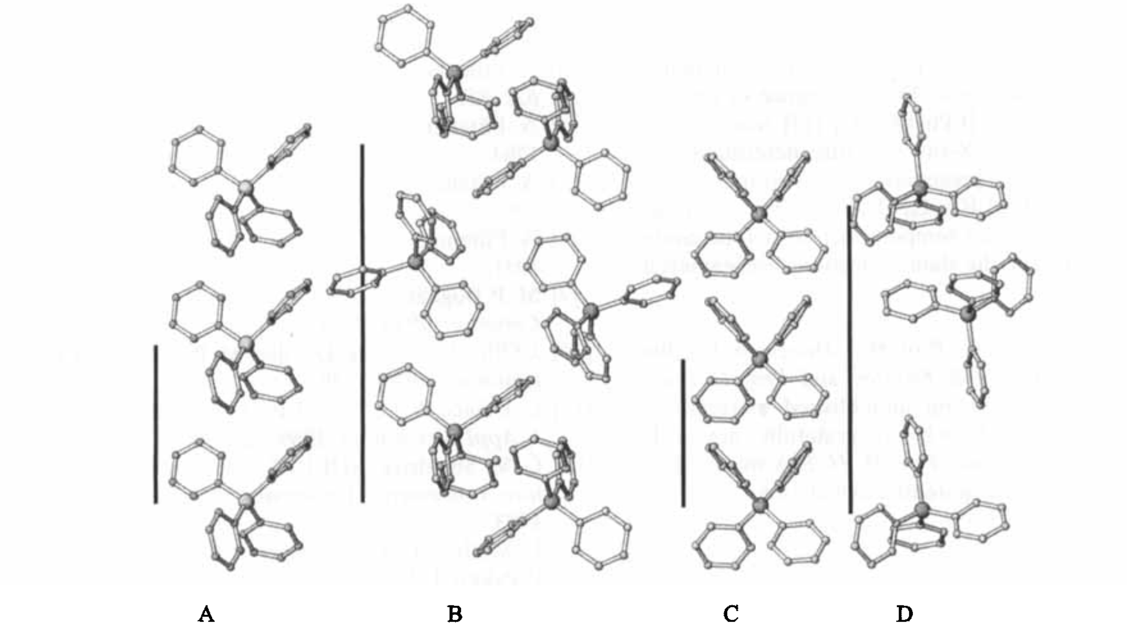

Fig. 4 $[PPh_4]^+$ columns in $[PPh_4]_2[Cu_2I_4]$ as seen perpendicular to the crystallographic *b*-axis. Letters denote the different modifications. Vertical bars indicate the translational period, which is 7.820 Å (**A**), 17.810 Å (**B**), 7.236 Å (**C**), and 15.941 Å (**D**). Data for **A** and **B** are taken from *Hartl* et al. [2 a].

this arrangement of the $[PPh_4]^+$ cations is a sufficient size of the monovalent anion. In Fig. 4 the arrangement of the $[PPh_4]^+$ ions in the four modifications of $[PPh_4]_2[Cu_2I_4]$, i. e. **A**, **B**, **C**, and **D**, is shown, data for **A** and **B** are taken from ref. [2 a]. For $[PPh_4]_2[Cu_2I_4]$ the situation is different from the compounds described in ref. [13] since the anion is divalent and thus a doubled number of cations is necessary to obtain charge balance. Nevertheless in those two modifications containing the planar $[Cu_2I_4]^{2-}$ ion, namely **A** and **C**, columns of $[PPh_4]^+$ ions are arranged in the way described by *Müller* [13], cf. Fig. 4. It becomes obvious, that the orientation of the phenyl rings is slightly different, i. e. they are rotated more or less along the P–C bonds. Thus for $[PPh_4]_2[Cu_2I_4]$-A two of four phenyl rings are oriented almost parallel to the *b*-axis whereas they fit each other in an optimised way in modification **C**. As a consequence the translational period along the columns is $b = 7.820$ Å for **A** compared to $b = 7.236$ Å for **C**. Packing of the $[PPh_4]^+$ ions is more complicated in case of those modifications containing the folded dianion $[Cu_2I_4]^{2-}$. They are not aligned along one axis derived from 4 but form a kind of zigzag chain for modification **D**. The stacking mode becomes obvious from Fig. 4. In this case the $[PPh_4]^+$ groups have one phenyl ring parallel to the *b*-axis. For one of the crystallographic different P atoms this ring tends up and for the other P atom down the *b*-axis. Thus the planes defined by the further three phenyl rings are oriented almost perpendicular to the *b*-axis. Two chains which are arranged in a different manner are interpenetrating for modification **B**, cf. Fig. 4. The $[PPh_4]^+$ columns are modified in the described way, because of the shape of the folded $[Cu_2I_4]^{2-}$ ions. Since the stacks are not as dense as for modification **A** and **C** there are some holes obtained in which the iodine atoms can be located.

Obviously the shape of the $[Cu_2I_4]^{2-}$ dianion in its compounds with $[PPh_4]^+$ as a counterion strongly depends on the three-dimensional arrangement in the described crystal structures, i. e. the shape of the $[Cu_2I_4]^{2-}$ dianion is strongly influenced by packing necessities. The relatively short distances *d*(Cu–Cu), e. g. *d*(Cu–Cu) = 2.550 Å found in modification **D**, can only be understood taking dispersion interactions into account [14]. However, slight enlargements of *d*(Cu–Cu) above the shortest possible value for a given folding angle, *vide supra*, remain to be explained.

4 Experimental

Bis-tetraphenylphosphonium-di-μ-iodo-diiodocuprate(I)-**B**, -**C** and -**D** were obtained by reacting freshly reduced copper pieces (2.54 g, 40 mmol), iodine (2.54 g, 20 mmol), and tetraphenylphosphoniumiodide (2.32 g, 5 mmol) under a nitrogen atmosphere in 100 ml of dry acetone. The reaction mixture is refluxed for 6 h and unreacted solids are filtered of from the hot solution. The solid residue is washed several times with dry acetone. The resulting solution is slowly evaporated at room temperature over a period of two weeks. When almost no more acetone is left, a mixture of pale yellow crystals of $[PPh_4]_2[Cu_2I_4]$-C, colourless crystals of $[PPh_4]_2[Cu_2I_4]$-D, colourless crystals of $[PPh_4]_2[Cu_2I_4]$-B [2 a], and dark brown crystals of $[PPh_4]I_3$ [16] can be isolated from the mother liquor. The compounds are almost insoluble in water and non polar organic solvents but may be recrystallised from acetone. The crystals can be distinguished by their typical shapes, viz. slender needles (**C**), flat plates (**D**), flat plates (**B**), and their colour, *vide supra*. The occurrence of crystals of $[PPh_4]_2[Cu_2I_4]$-A [2 a] or $[PPh_4][Cu_3I_4]$ [15] was not observed. Crystals suitable for X-ray structure determinations were characterised by precession photographs. For $[PPh_4]_2[Cu_2I_4]$-C and $[PPh_4]_2[Cu_2I_4]$-D X-ray diffraction datasets were collected at room temperature on a four circle diffractometer. Details for the data collections are gathered in Table 1.

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