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Preparation and molecular structures of two tetranuclear π complexes, with cubane Cu_4Cl_4-cores, between *endo*-dicyclopentadiene and copper(I) chloride

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Abstract

Two tetranuclear complexes, $[Cu_4Cl_4(C_{10}H_{12})_4]$ (**1** and **2**), containing distorted cubane Cu_4Cl_4 cores, between copper(I) chloride and *endo*-dicyclopentadiene have been prepared and their crystal structures determined. *endo*-Dicyclopentadiene coordinates to copper(I) via the double bond in the norbornene ring in both complexes, the copper(I) atom exhibiting distorted tetrahedral (trigonal pyramidal) coordination geometry. The Cu–C distances range from 2.011(16)–2.092(15) Å in **1** and from 2.051(9)–2.077(9) Å in **2**. Complex **2** can be described as a loose association of two $Cu_2Cl_2(C_{10}H_{12})_2$ dimers, with Cu–Cl bonds of 2.284(2)–2.323(3) Å, held together by long Cu $\cdots$ Cl interactions of 2.827(3) and 2.852(3) Å. The cubane core of the tetragonal complex **1** is also distorted, with Cu–Cl bonds in the range 2.274(4)–3.015(4) Å, but the distortion is such that no cube face is composed solely of short Cu–Cl bonds.

Introduction

Although *endo*-dicyclopentadiene acts as a tetrahapto ligand in a number of transition metal complexes [1], infrared spectroscopic studies of the 1 : 1 complex formed between *endo*-dicyclopentadiene and copper(I) chloride indicated that only one double bond was involved in complexation [2]. It was suggested [2] that the C=C bond involved was that in the cyclopentene ring of the molecule, but later evidence was interpreted in favour of coordination via the olefinic bond in the norbornene ring [3]. A subsequent infrared investigation showed that while the IR frequency associated with the double bond in the cyclopentene ring remained almost unperturbed on complexation, that corresponding to C=C in the norbornene ring was lowered by 100 cm^{-1}, providing strong evidence for norbornene complexation; the complex was, moreover, suggested to have a four-membered Cu_2Cl_2 core [4].

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Similar results with respect to coordination of dicyclopentadiene to copper(I) have been obtained for the 1 : 2 complex between copper(I) trifluoromethanesulfonate and *endo*-dicyclopentadiene, copper(I) here being shown to undergo *exo* complexation with the norbornene C=C double bonds of two dicyclopentadiene ligands [5]. Although the 1 : 1 complex formed between *endo*-dicyclopentadiene and copper(I) chloride has not been characterised crystallographically, it has been reported to crystallize with a tetragonal unit cell containing 32 formula units of $CuCl(C_{10}H_{12})$ [6]. In connection with a project directed towards the preparation of novel complexes between copper(I) chloride and conjugated and non-conjugated dienes [7], we have isolated the tetragonal phase of the 1 : 1 complex, obtained a further, orthorhombic, phase, and determined the crystal and molecular structures of both compounds.

Experimental

All operations were carried under nitrogen or argon by Schlenk techniques. Copper(I) chloride was purified as described in ref. 8, and dried in vacuo. Dicyclopentadiene (Aldrich, 95%) was deoxygenated and used without further purification. Tetrahydrofuran (Aldrich, anhydrous) was used as purchased.

Preparation of tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, 1)

Compound **1** was prepared by the method described by Schrauzer and Eichler [2]. Copper(I) chloride (0.5 g) was dissolved in 10 ml dicyclopentadiene by heating gently. When the solution was cooled to ambient temperature a white voluminous precipitate of **1** was formed. The precipitate was removed by filtration and the filtrate was allowed to evaporate slowly under nitrogen at room temperature. Colourless rods of **1** were deposited after a few days.

Preparation of tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (orthorhombic, 2)

Tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, **1**) (0.5 g), not completely purified from the dicyclopentadiene solvent, was dissolved in 20 ml tetrahydrofuran. The solution was allowed to evaporate slowly under nitrogen, and colourless prisms of **2** were deposited after a few days.

Infrared spectra. Spectra were recorded on a Mattson Polaris FTIR spectrometer, using Nujol mulls and CaF_2 windows (**1** and **2**) and a CaF_2 cell (dicyclopentadiene). For **1** bands at 1614 and 1471 cm^{-1} (ν(C=C)) and 1452, 1442 cm^{-1} ($\delta(CH_2)$) were obtained. Corresponding bands for **2** were 1613 and 1471 cm^{-1} (ν(C=C)) and 1456, 1440 cm^{-1} ($\delta(CH_2)$). The ligand itself exhibited bands at 1615 and 1572 cm^{-1} (ν(C=C)) and 1449 and 1439 cm^{-1} ($\delta(CH_2)$). The assignments involve the assumption that there is no coupling between stretching and bending modes.

Determination of the crystal and molecular structures of tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, 1 and orthorhombic, 2)

Crystal and intensity data. Owing to loss of dicyclopentadiene from the compounds, as well as sensitivity towards oxygen and water-vapour, the crystals were transferred to a Dewar vessel adapted for mounting crystals in glass capillaries at low temperature and an inert atmosphere. Single crystals, 0.30 × 0.20 × 0.15 mm (**1**), and, 0.30 × 0.20 × 0.20 mm (**2**), were thus sealed in a glass capillaries at

Table 1

Crystal data and experimental details for tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, **1** and orthorhombic, **2**)

	1	**2**
M_r	924.4	924.4
Unit-cell dimensions	a 21.258(5) c 18.758(10) Å V 8477(5) Å^3	a 18.151(7) b 10.494(3) c 19.617(9) Å V 3737(4) Å^3
Space group	$P\,4/ncc$ (No. 130) [9a]	$Pbcn$ (No. 60) [9a]
Z	8	4
D_c	1.45 g cm^{-3}	1.64 g cm^{-3}
μ(Mo-K_α)	22.7 cm^{-1}	25.7 cm^{-1}
Habit	Colourless rods	Colourless prisms
Crystal size	0.30×0.20×0.15 mm	0.30×0.20×0.20 mm
Temperature	-127 ± 1°C	-144 ± 1°C
2θ range	$3.5 < 2\theta < 50$°	$3.5 < 2\theta < 50$°
Scan mode	ω–2θ	ω–2θ
ω scan rate	8° min^{-1}	32° min^{-1}
Scan width	$(1.00 + 0.30 \tan\theta)$°	$(1.10 + 0.30 \tan\theta)$°
No. of independent reflections measured excluding those systematically absent	3725	3284
No. of observed reflections [$I > 3.0\,\sigma(I)$]	1438	1697
Method used to solve structure	Direct methods (MITHRIL) [10]; subsequent electron density calculations	Direct methods (MITHRIL) [10]; subsequent electron density calculations
No. of parameters refined	217	217
Reflections weighted according to	$[\sigma^2(F_o)]^{-1}$	$[\sigma^2(F_o)]^{-1}$
R	0.065	0.054
R_w	0.085	0.064
Max.; min residual electron density	1.50; -0.87 e Å^{-3}	0.92; -0.87 e Å^{-3}

approximately −150 °C and transferred, at the same temperature, to a Rigaku AFC6R diffractometer. Intensity data were measured for $3.5 < 2\theta < 50°$ at −127 ± 1 °C (**1**) and −144 ± 1 °C (**2**), using graphite-monochromated Mo-K_α radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The ω–2θ scan mode was employed, weak reflections ($I < 10\sigma(I)$) being rescanned twice and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time to background counting time being 2 : 1. Cell constants were obtained by least-squares refinement using the setting angles for 25 reflections in the range $27.9 < 2\theta < 38.8°$ (**1**) and $41.0 < 2\theta < 46.8°$ (**2**). Crystal data and further details concerning the measurement of intensities are given in Table 1.

Structure determination and refinement. The structures were solved by direct methods (MITHRIL) [10], and subsequent electron density calculations. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms, with those hydrogen atoms whose positions could be located unambiguously from a difference map (17 for **1** and 20 for **2**) included as fixed contributions ($B = B_{eq}$ of the carrying carbon atom), gave final residuals of $R = 0.065$ ($R_w = 0.085$) for **1** and $R = 0.054$ ($R_w = 0.064$) for **2**. Further details concerning the refinements are given in Table 1. Atomic scattering factors and anomalous disper-

Table 2

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[Cu_4Cl_4(C_{10}H_{12})_4]$ (tetragonal, 1) [a]

Atom	x	y	z	B_{eq} [b]
Cu(1)	0.56228(9)	0.01169(9)	0.3342(1)	2.25(9)
Cu(2)	0.65702(9)	0.05391(10)	0.2041(1)	2.4(1)
Cl(1)	0.5805(2)	−0.0189(2)	0.1786(2)	2.2(2)
Cl(2)	0.6516(2)	0.0719(2)	0.3249(2)	2.0(2)
C(1)	0.5316(7)	−0.0794(7)	0.3564(9)	2(1)
C(2)	0.5975(8)	−0.0751(7)	0.3593(8)	2(1)
C(3)	0.6151(6)	−0.0822(7)	0.4372(8)	2(1)
C(4)	0.6048(8)	−0.1495(7)	0.4558(8)	2(1)
C(5)	0.6318(9)	−0.1991(9)	0.4082(10)	4(1)
C(6)	0.5818(11)	−0.2291(8)	0.3729(11)	4(1)
C(7)	0.5196(10)	−0.2081(8)	0.3957(10)	4(1)
C(8)	0.5308(7)	−0.1554(9)	0.4541(10)	3(1)
C(9)	0.5104(7)	−0.0882(8)	0.4312(9)	2(1)
C(10)	0.5569(7)	−0.0499(7)	0.4726(7)	2(1)
C(11)	0.7175(7)	0.0649(7)	0.1171(7)	2(1)
C(12)	0.7330(7)	0.1041(8)	0.1753(9)	3(1)
C(13)	0.7969(9)	0.0817(9)	0.2040(9)	4(1)
C(14)	0.8459(8)	0.0979(11)	0.1428(11)	5(1)
C(15)	0.8456(8)	0.1638(11)	0.1119(11)	5(1)
C(16)	0.8296(9)	0.1578(11)	0.0385(13)	5(1)
C(17)	0.8198(9)	0.0911(11)	0.0168(9)	5(1)
C(18)	0.8290(8)	0.0490(9)	0.0822(9)	3(1)
C(19)	0.7673(8)	0.0146(8)	0.1105(8)	3(1)
C(20)	0.7883(7)	0.0101(9)	0.1908(9)	3(1)

[a] Estimated standard deviations are given in parentheses. [b] B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^\star a_j^\star \mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3

Fractional coordinates and equivalent isotropic thermal parameters (Å^2) for the non-hydrogen atoms in $[Cu_4Cl_4(C_{10}H_{12})_4]$ (orthorhombic, **2**) [a]

Atom	x	y	z	B_{eq} [b]
Cu(1)	0.92981(7)	0.3769(1)	0.80366(6)	2.89(6)
Cu(2)	0.92542(7)	0.1529(1)	0.70738(6)	2.58(5)
Cl(1)	0.9149(1)	0.3674(2)	0.6862(1)	2.3(1)
Cl(2)	0.9216(1)	0.1635(2)	0.8253(1)	2.5(1)
C(1)	0.9215(5)	0.5652(8)	0.8309(4)	2.3(4)
C(2)	0.9157(5)	0.4934(8)	0.8883(5)	2.7(5)
C(3)	0.8372(5)	0.5019(9)	0.9127(5)	3.1(5)
C(4)	0.8288(6)	0.6431(10)	0.9395(5)	3.6(5)
C(5)	0.8882(7)	0.6987(12)	0.9842(5)	4.2(6)
C(6)	0.9235(7)	0.8003(11)	0.9514(6)	4.6(6)
C(7)	0.8928(6)	0.8186(9)	0.8860(6)	3.5(5)
C(8)	0.8317(6)	0.7230(8)	0.8730(5)	2.9(5)
C(9)	0.8465(5)	0.6189(8)	0.8167(4)	2.3(4)
C(10)	0.7977(5)	0.5129(9)	0.8448(5)	2.8(5)
C(11)	0.9016(5)	0.0432(9)	0.6238(5)	2.5(4)
C(12)	0.9124(5)	−0.0354(7)	0.6795(5)	2.0(4)
C(13)	0.8378(5)	−0.0882(8)	0.6986(5)	2.2(4)
C(14)	0.8167(5)	−0.1844(9)	0.6413(5)	3.0(5)
C(15)	0.8748(7)	−0.2797(9)	0.6189(7)	5.0(7)
C(16)	0.8900(8)	−0.2460(15)	0.5469(10)	8(1)
C(17)	0.8546(7)	−0.1444(12)	0.5222(6)	4.6(6)
C(18)	0.8050(5)	−0.0966(10)	0.5789(5)	3.1(5)
C(19)	0.8205(5)	0.0408(9)	0.6083(4)	2.3(4)
C(20)	0.7875(5)	0.0230(8)	0.6797(4)	2.2(4)

[a] Estimated standard deviations are given in parentheses. [b] B_{eq} is defined as $\frac{8\pi^2}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

sion corrections were taken from ref. 9b; all calculations were performed using the TEXSAN [11] software package. Structural illustrations were drawn with ORTEP [12]. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2 and 3, and selected geometrical parameters in Tables 4 and 5. Lists of observed and calculated structure factors, fractional coordinates for the hydrogen atoms, C–H bond distances, and anisotropic thermal parameters for the non-hydrogen atoms may be obtained from the authors.

Discussion

Both the tetragonal (**1**) and the orthorhombic (**2**) phases of the 1 : 1 complexes between *endo*-dicyclopentadiene and copper(I) chloride contain discrete tetramers with distorted cubane or stellar quadrangular Cu_4Cl_4 cores. The molecular structures of **1** and **2** are illustrated in Figs. 1 and 2, and stereoviews of the complexes are given in Figs. 3 and 4. Tetrameric olefinic complexes of copper(I) chloride with "tub" [13] and "step" [14,15] Cu_4Cl_4 cores have been reported previously. The present complexes **1** and **2** exhibit cubane or stellar quadrangular cores of the type now relatively common in adducts between copper(I) chloride and phosphines or nitrogen-bases [16–19].

Table 4

Selected bond distances and angles in [$Cu_4Cl_4(C_{10}H_{12})_4$] (tetragonal, **1**). X(1) and X(2) are the midpoints of the C(1)–C(2) and C(11)–C(12) bonds, respectively. Symmetry code: (*i*): 1/2 + *y*, *x* − 1/2, 1/2 − *z*

Cu(1)–C(1)	2.085(15)	Cu(2)–C(11)	2.092(15)
Cu(1)–C(2)	2.046(15)	Cu(2)–C(12)	2.011(16)
Cu(1)–X	1.944	Cu(2)–X	1.926
Cu(1)–Cl(1)	3.015(4)	Cu(2)–Cl(1)	2.296(4)
Cu(1)–Cl(2)	2.297(4)	Cu(2)–Cl(2)	2.300(4)
Cu(1)–Cl(1^{i})	2.274(4)	Cu(2)–Cl(2^{i})	2.808(4)
C(1)–C(2)	1.40(2)	C(11)–C(12)	1.41(2)
C(2)–C(3)	1.52(2)	C(12)–C(13)	1.54(2)
C(3)–C(4)	1.49(2)	C(13)–C(14)	1.59(2)
C(4)–C(5)	1.50(2)	C(14)–C(15)	1.52(3)
C(5)–C(6)	1.40(2)	C(15)–C(16)	1.42(3)
C(6)–C(7)	1.46(3)	C(16)–C(17)	1.49(3)
C(7)–C(8)	1.58(2)	C(17)–C(18)	1.53(2)
C(8)–C(4)	1.58(2)	C(18)–C(14)	1.58(2)
C(8)–C(9)	1.55(2)	C(18)–C(19)	1.59(2)
C(9)–C(1)	1.48(2)	C(19)–C(11)	1.51(2)
C(9)–C(10)	1.50(2)	C(19)–C(20)	1.57(2)
C(10)–C(3)	1.56(2)	C(20)–C(13)	1.55(2)
Cu(1) ··· Cu(2)	3.288(3)	Cu(1) ··· Cu(2^{i})	3.177(3)
Cu(1) ··· Cu(1^{i})	3.505(4)	Cu(2) ··· Cu(2^{i})	3.545(4)
Cl(1^{i})–Cu(1)–X(1)	132.0	Cl(1)–Cu(2)–X(2)	130.1
Cl(2)–Cu(1)–X(1)	122.6	Cl(2)–Cu(2)–X(2)	122.4
Cl(1^{i})–Cu(1)–Cl(2)	105.1(1)	Cl(1)–Cu(2)–Cl(2)	106.1(1)
Cu(1^{i})–Cl(1)–Cu(2)	88.1(1)	Cu(1)–Cl(2)–Cu(2)	91.3(1)
C(2)–C(1)–C(9)	106(1)	C(12)–C(11)–C(19)	109(1)
C(1)–C(2)–C(3)	106(1)	C(11)–C(12)–C(13)	107(1)
C(2)–C(3)–C(4)	107(1)	C(12)–C(13)–C(14)	105(1)
C(2)–C(3)–C(10)	100(1)	C(12)–C(13)–C(20)	98(1)
C(4)–C(3)–C(10)	102(1)	C(14)–C(13)–C(20)	100(1)
C(3)–C(4)–C(5)	119(1)	C(13)–C(14)–C(15)	118(2)
C(3)–C(4)–C(8)	103(1)	C(13)–C(14)–C(18)	103(2)
C(5)–C(4)–C(8)	108(1)	C(15)–C(14)–C(18)	109(2)
C(4)–C(5)–C(6)	108(2)	C(14)–C(15)–C(16)	107(2)
C(5)–C(6)–C(7)	114(2)	C(15)–C(16)–C(17)	112(2)
C(6)–C(7)–C(8)	106(2)	C(16)–C(17)–C(18)	109(2)
C(7)–C(8)–C(4)	103(1)	C(17)–C(18)–C(14)	103(2)
C(7)–C(8)–C(9)	115(1)	C(17)–C(18)–C(19)	115(1)
C(4)–C(8)–C(9)	102(1)	C(14)–C(18)–C(19)	104(1)
C(8)–C(9)–C(10)	100(1)	C(18)–C(19)–C(20)	96(1)
C(8)–C(9)–C(1)	107(1)	C(18)–C(19)–C(11)	106(1)
C(1)–C(9)–C(10)	103(1)	C(11)–C(19)–C(20)	99(1)
C(9)–C(10)–C(3)	94(1)	C(19)–C(20)–C(13)	97(1)

The isomers differ in the nature of their cores. In **2** the Cu ··· Cl distances are elongated in the crystallographic *a* direction, i.e. Cu(1) ··· Cl(1^{i}) = 2.827(3) and Cu(2) ··· Cl(2^{i}) = 2.852(3) Å, the molecule thus being most appropriately described as a loose association of two dimeric $Cu_2Cl_2(C_{10}H_{12})_2$ units. Similar, but less pronounced distortion has been noted for [$Cu_4Cl_4(PPh_3)_4$] [16], [$Cu_4Br_4(PPh_3)_4$] [18] and [Cu_4Cl_4(tmspy)$_4$], (tmspy = 2-[bis(trimethylsilyl)methyl]pyridine) [17]. Dis-

Table 5

Selected bond distances and angles in $[Cu_4Cl_4(C_{10}H_{12})_4]$ (orthorhombic, **2**). X(1) and X(2) are the midpoints of the C(1)–C(2) and C(11)–C(12) bonds, respectively. Symmetry code: (i): $2-x$, y, $3/2-x$

Cu(1)–C(1)	2.052(8)	Cu(2)–C(11)	2.051(9)
Cu(1)–C(2)	2.077(9)	Cu(2)–C(12)	2.064(8)
Cu(1)–X(1)	1.950	Cu(2)–X(2)	1.938
Cu(1)–Cl(1)	2.323(3)	Cu(2)–Cl(1)	2.297(2)
Cu(1)–Cl(2)	2.284(2)	Cu(2)–Cl(2)	2.317(3)
Cu(1)–Cl(1 ^{i})	2.827(3)	Cu(2)–Cl(2 ^{i})	2.852(3)
C(1)–C(2)	1.359(12)	C(11)–C(12)	1.383(12)
C(2)–C(3)	1.506(13)	C(12)–C(13)	1.510(11)
C(3)–C(4)	1.580(13)	C(13)–C(14)	1.558(12)
C(4)–C(5)	1.508(15)	C(14)–C(15)	1.518(14)
C(5)–C(6)	1.400(16)	C(15)–C(16)	1.483(20)
C(6)–C(7)	1.411(15)	C(16)–C(17)	1.336(20)
C(7)–C(8)	1.517(13)	C(17)–C(18)	1.516(14)
C(8)–C(4)	1.552(12)	C(18)–C(14)	1.546(13)
C(8)–C(9)	1.577(12)	C(18)–C(19)	1.578(12)
C(9)–C(1)	1.500(12)	C(19)–C(11)	1.504(13)
C(9)–C(10)	1.525(12)	C(19)–C(20)	1.533(12)
C(10)–C(3)	1.517(14)	C(20)–C(13)	1.526(11)
Cu(1) ··· Cu(2)	3.016(2)	Cu(1) ··· Cu(2 ^{i})	3.532(2)
Cu(1) ··· Cu(1 ^{i})	3.305(3)	Cu(2) ··· Cu(2 ^{i})	3.182(2)
Cl(1)–Cu(1)–X(1)	125.6	Cl(1)–Cu(2)–X(2)	132.4
Cl(2)–Cu(1)–X(1)	133.8	Cl(2)–Cu(2)–X(2)	126.7
Cl(1)–Cu(1)–Cl(2)	97.75(9)	Cl(1)–Cu(2)–Cl(2)	97.53(9)
Cu(1)–Cl(1)–Cu(2)	81.55(9)	Cu(1)–Cl(2)–Cu(2)	81.92(9)
C(2)–C(1)–C(9)	106.0(8)	C(12)–C(11)–C(19)	105.9(8)
C(1)–C(2)–C(3)	106.8(8)	C(11)–C(12)–C(13)	105.6(8)
C(2)–C(3)–C(4)	104.8(8)	C(12)–C(13)–C(14)	106.6(7)
C(2)–C(3)–C(10)	100.5(8)	C(12)–C(13)–C(20)	101.7(6)
C(4)–C(3)–C(10)	100.1(8)	C(14)–C(13)–C(20)	100.1(7)
C(3)–C(4)–C(5)	199.2(9)	C(13)–C(14)–C(15)	117.6(9)
C(3)–C(4)–C(8)	102.9(8)	C(13)–C(14)–C(18)	102.6(7)
C(5)–C(4)–C(8)	110.1(10)	C(15)–C(14)–C(18)	104.8(9)
C(4)–C(5)–C(6)	110.7(10)	C(14)–C(15)–C(16)	104.7(11)
C(5)–C(6)–C(7)	110.1(12)	C(15)–C(16)–C(17)	116.2(12)
C(6)–C(7)–C(8)	110.6(10)	C(16)–C(17)–C(18)	106.8(12)
C(7)–C(8)–C(4)	103.6(9)	C(17)–C(18)–C(14)	107.4(9)
C(7)–C(8)–C(9)	116.8(8)	C(17)–C(18)–C(19)	117.7(8)
C(4)–C(8)–C(9)	102.9(7)	C(14)–C(18)–C(19)	103.5(7)
C(8)–C(9)–C(10)	98.8(7)	C(18)–C(19)–C(20)	98.8(7)
C(8)–C(9)–C(1)	106.7(8)	C(18)–C(19)–C(11)	105.4(8)
C(1)–C(9)–C(10)	101.3(7)	C(11)–C(19)–C(20)	102.3(7)
C(9)–C(10)–C(3)	96.0(7)	C(19)–C(20)–C(13)	94.9(7)

tortion of the cube towards a stellar quadrangular configuration is apparent from Figs. 2 and 4. The core of **1** is distorted such that there is no cube face which is composed of four short Cu–Cl bonds (cf. Table 4 and Fig. 1) and, if the long Cu(1)–Cl(1) or Cu(2)–Cl(2^i) contacts of 3.015(4) and 2.808(4) Å (symmetry code (i): $1/2+y$, $x-1/2$, $1/2-z$) are disregarded, the core can be seen as a "tub" similar to that in the complex between norbornadiene and CuCl, $[Cu_4Cl_4(C_7H_8)]$

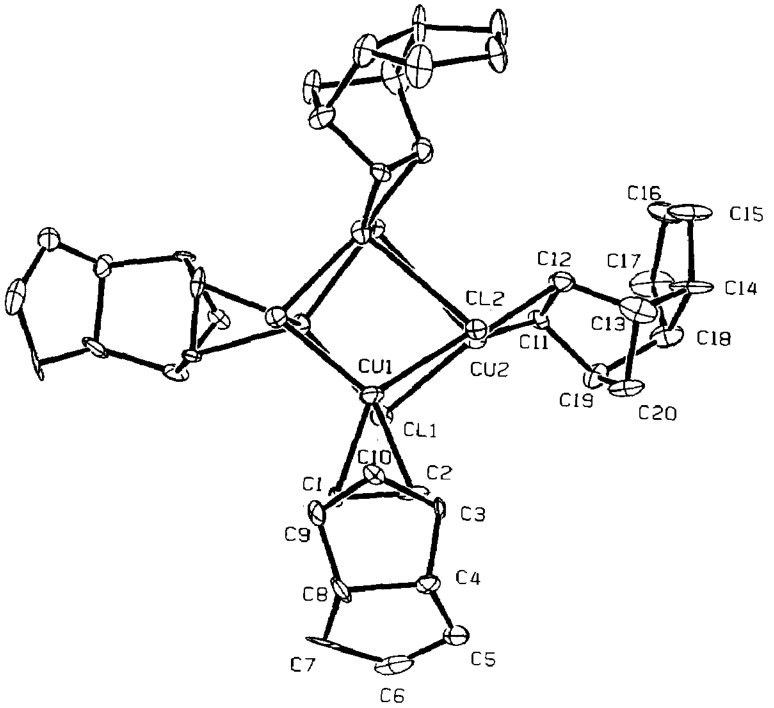

Fig. 1. Tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, 1) showing the crystallographic numbering. The thermal ellipsoids enclose 30% probability.

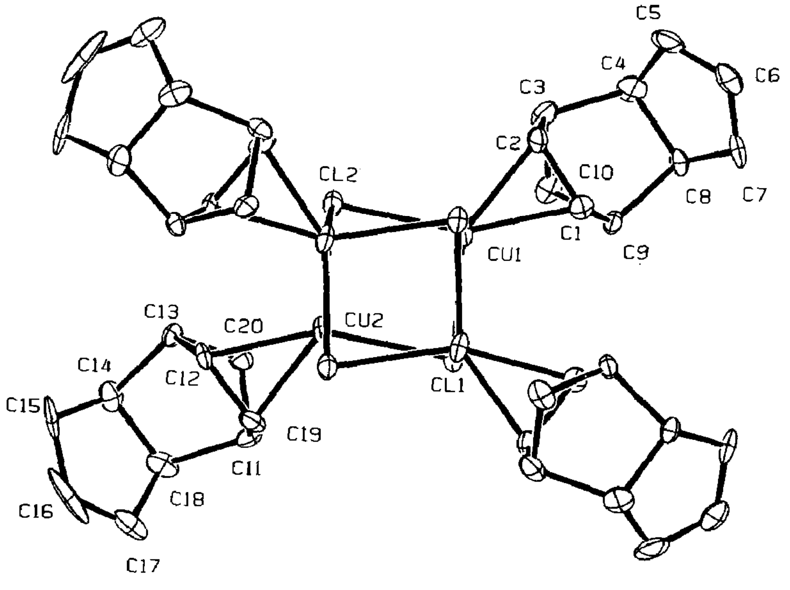

Fig. 2. Tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (orthorhombic, 2) showing the crystallograpic numbering. The thermal ellipsoids enclose 30% probability.

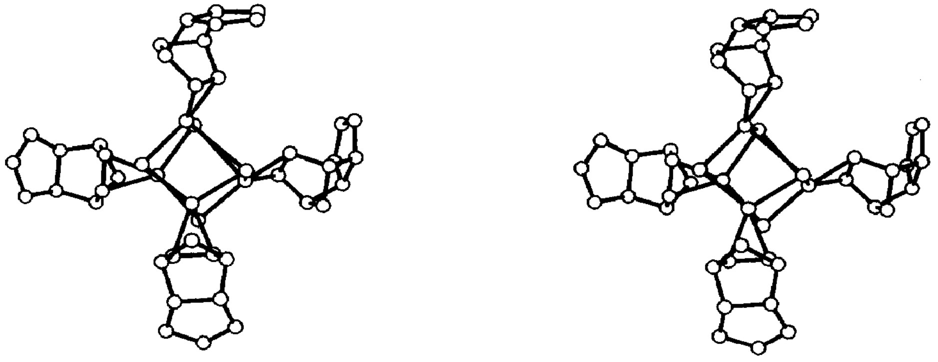

Fig. 3. Stereoview of tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (tetragonal, 1).

[13]. As can be seen from Figs. 3 and 4, the core of **1** shows less distortion towards the stellar quadrangular configuration than does that of **2**.

The infrared frequencies shown by the two compounds are in good agreement with one another, and also with those values determined previously [4]. As expected, *endo*-dicyclopentadiene coordinates to copper(I) via the C=C double bond in the norbornene ring in both complexes. The Cu–C distances lie within the range reported for π-olefinic complexes of copper(I) (see e.g. refs. 20–21, and references therein), and there are slight, but not significant, lengthenings of the C=C double bonds. The copper(I) atoms all exhibit distorted tetrahedral (trigonal pyramidal) coordination, with the olefin and two chloride ligands in the trigonal plane and a fourth chloride ligand at 2.8–3.0 Å, the copper(I) atoms in **1** being displaced by 0.07 and 0.13 Å from the trigonal plane in the direction of the apical chloride ligands; the corresponding displacements in **2** are 0.20 and 0.22 Å. The inequality of the Cl–Cu–X angles associated with both copper(I) centres in the two complexes, where X is the midpoint of the norbornene C=C, (cf. Tables 4 and 5), suggest that there is olefin-sliding [22] in the trigonal plane. For neither complex was it possible to locate the double bond of the cyclopentene ring, there being disorder associated with C(5), C(6), C(7) and C(15), C(16), C(17), as is apparent from the C–C distances and the thermal ellipsoids for these atoms.

The most striking difference between molecules **1** and **2** lies in the mutual orientation of the four dicyclopentadiene ligands. In **2**, which can be regarded as a loose association of dimeric entities, ligands *trans* to one another are related by an approximate 2-fold axis (Figs. 2 and 4), such that two Cu–X linkages each lie

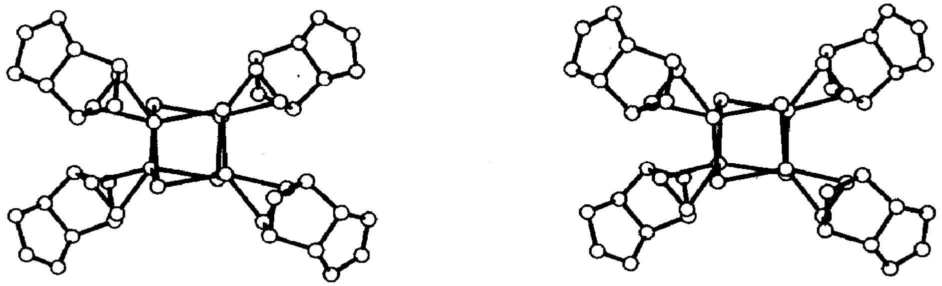

Fig. 4. Stereoview of tetra-μ-chloro-tetrakis[dicyclopentadienecopper(I)] (orthorhombic, 2).

approximately along the diagonals of the faces of the core perpendicular to the crystallographic *a* direction. In **1** the ligands are twisted relative one another such that each Cu–X linkage is parallel to a diagonal of a different face of the Cu_4Cl_4 cube, these four faces circumscribing the cubane core (Figs. 1 and 3).

The molecular geometries, and in particular, the relative location of the short Cu–Cl distances within the two cores suggests that whereas the tetragonal phase is likely to exist as a tetramer in solution, the orthorhombic phase (**2**) probably dissociates into dimers in solution. Since copper(I) would be coordinatively unsaturated in the latter species, it is not inconceivable that **2** may prove to be a useful starting material for the preparation of mixed π-acid ligand complexes of copper(I).

The complexes between dicyclopentadiene and copper(I) chloride, although unstable with respect to loss of ligand, are considerably more stable than e.g. [Cu(CO)Cl] [23], and complexes between α,β-unsaturated carbonyl compounds [21] or dienes [7] and CuCl, in which the copper-chloride framework is polymeric. The resistance of $[CuCO(O^tBu)]_4$, which has a cubane Cu_4O_4 core, to decarbonylation has been attributed to its kinetic stability, i.e. to the unfavourable pyramidal coordination geometry for copper(I) that would be present in the initial decarbonylation product [24]. The relative stability of the tetrameric complexes between copper(I) and dicyclopentadiene with respect to loss of the diene can be attributed to a mechanism similar to that described for $[CuCO(O^tBu)]_4$ [24]. In complexes prone to loss of ligand that contain polymeric Cu-Cl frameworks, on the other hand, proximity of chloride ligands to an initially pyramidal metal centre formed during decomposition promote tetrahedral coordination by chloride, the final decomposition product being solid CuCl. A further factor contributing to the relative stability of the complexes between dicyclopentadiene and copper(I) chloride may be ring strain, the stability constants of complexes between *endo*-cycloolefins and silver(I) having been found to increase with increase in ring strain within the ligand [3,25].

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