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METAL π-COMPLEXES OF CYCLOOCTATETRAENES

V *. SYNTHESIS AND X-RAY ANALYSIS OF TETRAMERIC DIBENZO[*a*,*e*]CYCLOOCTATETRAENECOPPER(I) CHLORIDE, A NEW "STEP" CONFIGURATION FOR THE Cu_4Cl_4 RING

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Summary

Tetrameric dibenzo[*a*,*e*]cyclooctatetraenecopper(I) ★, $[(C_{16}H_{12})CuCl]_4$, **1**, has been synthesized and characterized by X-ray crystallography. Complex **1** crystallizes in space group $P\bar{1}$ with a 9.287(7), b 10.818(7), c 13.234(5) Å, α 91.34(4), β 103.44(4), γ 95.20(5)°, V 1287(1) Å^3, and $Z = 1$. The structure has been refined to $R_F = 0.063$ and $R_{wF} = 0.078$ for 3286 observed Mo-K_α data and 325 variables. The cyclic molecule, which has crystallographically imposed $\bar{1}$ symmetry, consists of an eight-membered ring of alternating Cu and Cl atoms in a "step" (or "chair") configuration, with an organic ligand π-bonded to each metal center via a pair of olefinic double bonds. The two symmetry-independent copper(I) atoms are in distorted trigonal pyramidal coordination, each being bound asymmetrically to chloride and olefin ligands at distances in the ranges 2.263(2)–2.278(2) and 2.099(5)–2.801(6) Å, respectively.

Introduction

The copper(I) halide complexes LM^IX (M = Ag and Cu; X = Cl, Br, and I; L = unidentate tertiary phosphines and arsines, and nitrogen donor ligands such as piperidine, pyridine, and morpholine) occur in the crystalline state frequently as tetrameric cluster systems, each possessing a M_4X_4 core in either a distorted "cubane-like" configuration (I) or a "step" (also described as "chair") configuration

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[★] IUPAC name: cyclotetra-μ-chlorotetrakis[9–10 : 11–12-η-dibenzo[*a*,*e*]cyclooctenecopper(I)] [2].

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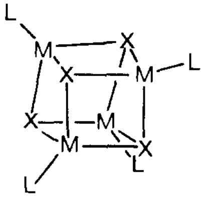
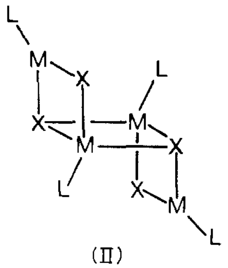
(II) [3–5]. These two structural types differ in the number of triply bridging halogen ligands and the mode of coordination about the metal centers. The complexes $[(Ph_2PCH_2PPh_2)_2Cu_4X_4]$ (X = Cl, Br, and I), though crystallizing in different space groups, have been shown to possess a common centrosymmetric Cu_4X_4 core in the "step" configuration, which is undoubtedly stabilized by the bite of the bidentate diphosphino ligand [6]. It is noteworthy that a third possible structure for the M_4X_4 core, namely the "tub" (or "boat") configuration, has not yet been observed, presumably due to unfavorable repulsion between the bulky pnicogen ligands.

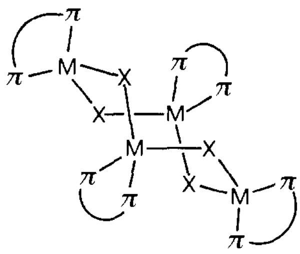


(I)

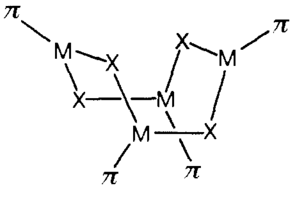


(II)

Steric overcrowding in a "step" structure (II) can be considerably relieved by cleaving the two M-X "cross links" to yield a M_4X_4 ring in which all halogen atoms merely play a doubly bridging role. Such an eight-membered ring of alternating M and X atoms is capable of existing in both a "tub" form (III) and a "step" form (IV). In fact, an example of a "tub-shaped" Cu_4Cl_4 ring was discovered almost two decades ago in an X-ray analysis of $[(norbornadiene)CuCl]_4$, **2**, in which only one double bond of the diolefin π-bonds to each metal atom in an *exo* fashion to give a distorted trigonal planar coordination [7].



(IV)



(III)

Following our recent report of a metal π-complex, benzocyclooctatetraene·$AgClO_4$, containing both arene and olefin ligands coordinated simultaneously to a silver(I) ion [1], we embarked on a search for an analogous copper(I) species by reducing an ethanol solution of dibenzo[*a*,*e*]cyclooctatetraene *, **3**, and copper(II) chloride with sulfur dioxide [8]. For the resulting crystalline product of stoichiometry $C_{16}H_{12}CuCl$, we anticipated a dimeric structure like that of $[(1,5\text{-cyclooctadiene})CuCl]_2$ [9], or a polymeric one similar to the single chain in $[(cyclooctatetraene)CuCl]_n$, **4**, [10], or the (different) double chains in $[(CH_3NC)CuI]_n$ [11] and $[(CH_3CN)CuX]_n$ (X = Cl and Br) [12]. However, an X-ray analysis revealed instead, serendipitously, a discrete centrosymmetric $[(C_{16}H_{12})CuCl]_4$ tetramer, **1**, comprising a Cu_4Cl_4 ring in the hitherto unobserved (to our knowledge) "step" conformation

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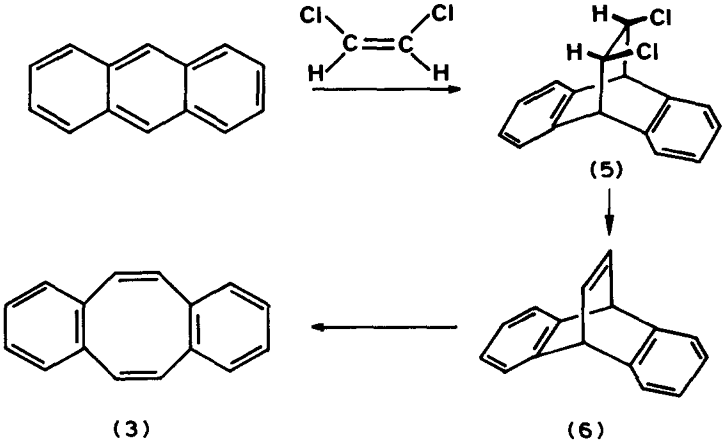
* IUPAC name: dibenzo[*a*,*e*]cyclooctene [2].

conformation (IV), with each metal atom coordinated exocyclically by both olefinic double bonds of organic ligand **3**.

Experimental

Synthesis of dibenzo[a,e]cyclooctatetraene, 3

Compound **3** was synthesized via a three-step route according to the following scheme [13].



The reaction between anthracene and *cis*-1,2-dichloroethylene at 240°C for 24 h in a sealed tube [14] gave a 70% yield of the condensation product *cis*-2,3-dichlorodibenzobicyclo[2.2.2]octadiene, **5**, m.p. 207°C, lit. 203–204°C [14]. The dichloride **5** was subjected to dechlorination with sodium in boiling n-amyl alcohol [14,15] to furnish dibenzobicyclo[2.2.2]octatriene, **6**, in 90% yield, m.p. 117–119°C, lit. 119–120°C [15]. Irradiation of **6** in tetrahydrofuran [16] for 24 h gave colorless crystals of **3** in 75% yield, m.p. 104°C, lit. 105–107°C [16]; ^{1}H NMR ($CDCl_3$): τ 2.91 (m, AA′BB′, 8H) and τ 3.25 (s, 4H).

Preparation of cyclo-tetra-μ-chloro-tetrakis[9–10 : 11–12-η-dibenzo[a,e]cyclooctene-copper(I)], 1

Compound **3** (7.4 mmol) and $CuCl_2 \cdot 2H_2O$ (10 mmol) were dissolved in 15 ml 95% ethanol. The resulting pale green solution was cooled in an ice-water bath, and SO_2 gas was bubbled into it until a suspension initially appeared. The reaction mixture was then kept in the icewater bath for 3 h, after which it turned clear and a crop of pale-yellow crystals of **1** settled at the bottom. The crystals were filtered, washed with ice-cooled methanol, and dried in a desiccator. Compound **1** melts with decomposition at 210°C.

X-Ray analysis

A selected crystal (0.36 × 0.36 × 0.16 mm) was mounted on a Nicolet R3m automatic diffractometer. Standard centering and auto-indexing procedures [17] indicated a primitive triclinic lattice. The orientation matrix and accurate unit-cell dimensions were determined from a least-squares fit of 21 reflections ($10° < 2\theta < 23°$). Intensity data were collected at 22°C (details summarized in Table 1). Three

TABLE 1

DATA COLLECTION AND PROCESSING PARAMETERS

Molecular formula	$[(C_{16}H_{12})CuCl]_4$
Molecular weight	1213.09
Cell constants	a 9.287(7), b 10.818(7), c 13.234(5) Å, α 91.34(4), β 103.44(4), γ 95.20(5)°, V 1287(1) Å^3, $Z = 1$
Density	D_c 1.565, D_m 1.567 g cm^{-3}
Space group	$P\bar{1}$
Radiation	graphite-monochromatized MoK_α, λ 0.71069 Å
Absorption coefficient	18.87 cm^{-1}
Mean μr	0.22
Transmission factors	0.525–0.736
Scan type and speed	$\omega/2\theta$; 2.55–8.37 deg min^{-1}
Scan range	1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$
Background counting	stationary counts for 1/2 of scan time at each end of scan
Collection range	h, $\pm k$, $\pm l$; $2\theta_{max}$ 50°
No. of unique data measured	3963
Observed data with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$, n	3286
No. of variables, p	325
$R_F = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.063
Weighting scheme	$w = [\sigma^2(\lvert F_o\rvert)+0.0005\lvert F_o\rvert^2]^{-1}$
$R_{wF} = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.078
Goodness of fit, $S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.959

standard reflections ($1\ \bar{2}\ \bar{2}$, $1\ \bar{3}\ \bar{2}$, and $\bar{1}\ 3\ 2$) monitored every 125 reflection measurements fluctuated within ±2% of their mean values. Empirical absorption correction was applied by a pseudo-ellipsoidal treatment of intensities of selected strong reflections measured at different azimuthal (ψ) angles [18–20]. Redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values following corrections for Lorentz and polarization factors.

Direct phase determination in space group $P\bar{1}$ (favored by intensity statistics) revealed the positions of two Cu and two Cl atoms in the asymmetric unit. The remaining non-hydrogen atoms were located from subsequent difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The 24 H atoms were generated on the basis of sp^2 hybridization (C–H 0.96 Å) of their respective parent C atoms and were assigned a common isotropic temperature factor of U_{iso} 0.06 Å^2. The final difference map showed residual extrema at 2.70 to -2.24 e Å^{-3}, with the highest peaks lying in the neighbourhood of the Cu atoms.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [18]. Analytical expressions [21] of neutral-atom scattering factors [22] were employed, and anomalous dispersion corrections [23] were incorporated. Blocked-cascade least-squares refinement [18,24] of 325 parameters coverged to the R indices listed in Table 1. Positional and thermal parameters of the non-hydrogen atoms are listed in Table 2 in accordance with the

(Continued on p. 130)

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a] (Å^2 $\times 10^4$ for Cu; $\times 10^3$ for other atoms)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu(1)	0.17325(13)	0.41429(8)	0.47962(6)	1117(9)	349(5)	301(5)	25(4)	67(5)	193(5)	598(4)
Cu(2)	−0.12847(8)	0.42277(8)	0.27317(6)	375(5)	482(5)	302(4)	−54(3)	53(3)	10(4)	394(3)
Cl(1)	0.1224(2)	0.4623(2)	0.3103(1)	36(1)	65(1)	30(1)	10(1)	5(1)	1(1)	44(1)
Cl(2)	−0.2111(2)	0.4054(1)	0.4219(1)	44(1)	36(1)	37(1)	−4(1)	13(1)	4(1)	38(1)
C(1)	0.5082(7)	0.2890(6)	0.7522(5)	37(4)	43(4)	39(4)	−10(3)	2(3)	7(3)	41(2)
C(2)	0.4807(8)	0.2362(7)	0.8387(5)	68(5)	52(5)	39(4)	−3(3)	−4(4)	22(4)	55(3)
C(3)	0.3373(8)	0.1933(7)	0.8412(5)	75(5)	50(4)	31(4)	7(3)	11(4)	6(4)	52(3)
C(4)	0.2216(8)	0.2080(6)	0.7567(5)	55(4)	48(4)	35(4)	2(3)	17(3)	2(3)	45(3)
C(5)	0.2493(7)	0.2592(5)	0.6663(4)	39(3)	24(3)	29(3)	−4(2)	7(3)	6(3)	31(2)
C(6)	0.1185(6)	0.2742(5)	0.5794(5)	32(3)	26(3)	37(3)	3(5)	9(3)	1(3)	32(2)
C(7)	0.0921(7)	0.2205(5)	0.4823(3)	34(3)	30(3)	32(3)	5(3)	5(3)	−2(3)	33(2)
C(8)	0.1896(7)	0.1378(5)	0.4444(4)	45(4)	24(3)	25(3)	3(3)	11(3)	3(3)	34(2)
C(9)	0.1267(8)	0.0183(6)	0.4070(5)	66(5)	41(4)	34(4)	−6(3)	11(3)	−3(3)	48(3)
C(10)	0.2110(9)	−0.0641(7)	0.3728(6)	88(6)	39(4)	47(4)	−11(3)	15(4)	1(4)	58(3)
C(11)	0.3562(9)	−0.0270(7)	0.3699(5)	93(6)	45(4)	41(4)	−6(3)	22(4)	28(4)	57(3)
C(12)	0.4158(8)	0.0911(7)	0.4027(5)	65(5)	56(5)	37(4)	2(3)	21(4)	19(4)	50(3)
C(13)	0.3351(7)	0.1757(5)	0.4424(4)	50(4)	32(3)	25(3)	0(3)	10(3)	9(3)	35(2)

C(14)	0.4107(7)	0.3017(6)	0.4765(5)	36(3)	39(4)	41(4)	10(3)	17(3)	6(3)	37(2)
C(15)	0.4355(6)	0.3545(5)	0.5713(5)	31(3)	29(3)	48(4)	1(3)	13(3)	−3(3)	36(2)
C(16)	0.3947(6)	0.2992(5)	0.6633(4)	33(3)	27(3)	35(3)	−6(3)	4(3)	7(3)	32(2)
C(17)	−0.5386(8)	0.1338(6)	0.1627(5)	68(5)	34(4)	40(4)	3(3)	20(3)	0(3)	46(2)
C(18)	−0.6820(8)	0.1672(7)	0.1278(5)	46(4)	57(5)	50(4)	−3(4)	15(3)	−15(4)	52(3)
C(19)	−0.7030(8)	0.2866(7)	0.1035(6)	39(4)	49(4)	65(5)	0(4)	14(3)	−7(3)	52(3)
C(20)	−0.5839(7)	0.3734(6)	0.1126(5)	43(4)	38(4)	50(4)	0(3)	12(3)	6(3)	43(2)
C(21)	−0.4373(7)	0.3428(5)	0.1469(4)	37(3)	32(3)	29(3)	−6(3)	7(3)	3(3)	33(2)
C(22)	−0.3183(6)	0.4441(5)	0.1554(4)	33(3)	29(3)	31(3)	−4(3)	4(3)	2(3)	32(2)
C(23)	−0.1952(6)	0.4478(6)	0.1122(4)	32(3)	36(3)	26(3)	−1(3)	−3(3)	7(3)	33(2)
C(24)	−0.1569(6)	0.3477(5)	0.0473(4)	23(3)	30(3)	27(3)	0(2)	2(2)	0(2)	28(2)
C(25)	−0.1366(6)	0.3781(5)	0.0512(4)	26(3)	33(3)	34(3)	6(3)	4(3)	−1(3)	32(2)
C(26)	−0.1055(7)	0.2899(6)	−0.1178(5)	36(3)	48(4)	30(3)	0(3)	10(3)	3(3)	38(2)
C(27)	−0.0919(7)	0.1689(6)	−0.0865(5)	45(4)	39(4)	36(4)	−5(3)	12(3)	6(3)	39(2)
C(28)	−0.1060(7)	0.1393(6)	0.0115(5)	37(3)	33(3)	40(4)	3(3)	8(3)	10(3)	37(2)
C(29)	−0.1387(6)	0.2261(5)	0.0792(4)	29(3)	30(3)	28(3)	0(2)	3(2)	5(2)	29(2)
C(30)	−0.1473(7)	0.1870(5)	0.1851(5)	39(2)	27(3)	34(3)	7(3)	5(3)	4(3)	34(2)
C(31)	−0.2682(7)	0.1816(5)	0.2220(5)	52(4)	29(3)	27(3)	6(3)	12(3)	6(3)	36(2)
C(32)	−0.4139(7)	0.2200(6)	0.1738(4)	41(4)	37(4)	26(3)	−2(3)	12(3)	0(2)	34(2)

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[a] Anisotropic temperature factor exponent takes the form: $-2\pi^2\Sigma\Sigma \mathbf{a}_i^* \cdot \mathbf{a}_j^* h_i h_j U_{ij}$. U_{eq} is the equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

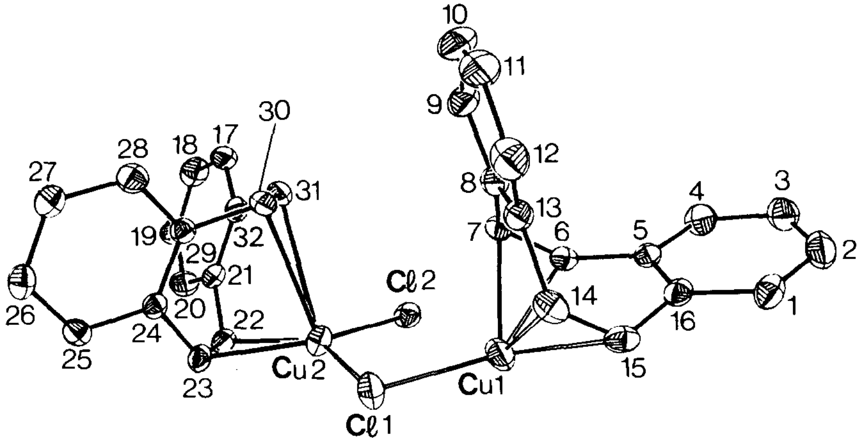

Fig. 1. Atom labelling in the asymmetric unit of complex **1**.

TABLE 3

BOND LENGTHS (Å), BOND ANGLES (deg) AND SELECTED TORSION ANGLES (deg)[a],[b]

(i) Around atoms of the Cu_4Cl_4 ring			
Cu(1)–Cl(1)	2.263(2)	Cu(2)–Cl(1)	2.265(2)
Cu(1)–Cl(2)^{I}	2.274(2)	Cu(2)–Cl(2)	2.278(2)
Cu(1)–C(6)	2.137(6)	Cu(2)–C(22)	2.099(5)
Cu(1)–C(7)	2.167(6)	Cu(2)–C(23)	2.107(6)
Cu(1)–C(14)	2.622(7)	Cu(2)–C(30)	2.753(6)
Cu(1)–C(15)	2.602(6)	Cu(2)–C(31)	2.801(6)
Cu(1)-π_1	2.042(6)	Cu(2)-π_3	1.985(5)
Cu(1)-π_2	2.526(7)	Cu(2)-π_4	2.697(6)
Cl(1)–Cu(1)–Cl(2)^{I}	108.0(1)	Cl(1)–Cu(2)–Cl(2)	110.7(1)
Cl(1)–Cu(1)-π_1	123.7(2)	Cl(1)–Cu(2)-π_3	122.7(2)
Cl(1)–Cu(1)-π_2	108.6(2)	Cl(1)–Cu(2)-π_4	109.9(1)
Cl(2)^{I}–Cu(1)-π_1	123.0(2)	Cl(2)–Cu(2)-π_3	124.6(2)
Cl(2)^{I}–Cu(1)-π_2	103.8(1)	Cl(2)–Cu(2)-π_4	96.2(1)
π_1-Cu(1)-π_2	82.2(2)	π_3-Cu(2)-π_4	79.3(2)
Cu(1)–Cl(1)–Cu(2)	98.8(1)	Cu(1)^{I}–Cl(2)–Cu(2)	113.4(1)
(ii) DBCOT A			
C(16)–C(1)	1.399(8)	C(8)–C(9)	1.399(8)
C(1)–C(2)	1.358(10)	C(9)–C(10)	1.372(11)
C(2)–C(3)	1.378(11)	C(10)–C(11)	1.382(12)
C(3)–C(4)	1.383(9)	C(11)–C(12)	1.365(10)
C(4)–C(5)	1.397(9)	C(12)–C(13)	1.400(10)
C(5)–C(16)	1.390(9)	C(13)–C(8)	1.382(9)
C(5)–C(6)	1.489(8)	C(13)–C(14)	1.485(8)
C(6)–C(7)	1.357(8)	C(14)–C(15)	1.327(9)
C(7)–C(8)	1.486(9)	C(15)–C(16)	1.481(9)
C(15)–C(16)–C(1)	118.1(5)	C(7)–C(8)–C(9)	117.0(6)
C(5)–C(16)–C(1)	118.6(5)	C(13)–C(8)–C(9)	120.1(6)
C(16)–C(1)–C(2)	121.8(6)	C(8)–C(9)–C(10)	120.3(7)
C(1)–C(2)–C(3)	119.9(6)	C(9)–C(10)–C(11)	120.0(7)
C(2)–C(3)–C(4)	119.7(7)	C(10)–C(11)–C(12)	119.6(8)
C(3)–C(4)–C(5)	120.7(7)	C(11)–C(12)–C(13)	121.8(7)

TABLE 3 (continued)

(ii) DBCOT A			
C(4)–C(5)–C(16)	117.5(6)	C(12)–C(13)–C(8)	118.0(6)
C(4)–C(5)–C(6)	119.1(5)	C(12)–C(13)–C(14)	117.5(6)
C(16)–C(5)–C(6)	123.3(5)	C(8)–C(13)–C(14)	124.5(6)
C(5)–C(6)–C(7)	125.8(6)	C(13)–C(14)–C(15)	126.3(6)
C(6)–C(7)–C(8)	125.8(5)	C(14)–C(15)–C(16)	126.8(5)
C(7)–C(8)–C(13)	122.8(5)	C(15)–C(16)–C(5)	123.3(5)
C(5)–C(6)–C(7)–C(18)	−0.8(10)	C(13)–C(14)–C(15)–C(16)	0.5(11)
C(6)–C(7)–C(8)–C(13)	−60.1(9)	C(14)–C(15)–C(16)–C(5)	−59.2(9)
C(7)–C(8)–C(13)–C(14)	−0.6(9)	C(15)–C(16)–C(5)–C(6)	−3.5(9)
C(8)–C(13)–C(14)–C(15)	61.5(9)	C(16)–C(5)–C(6)–C(7)	63.7(8)
*(iii) DBCOT **B***			
C(32)–C(17)	1.397(9)	C(24)–C(25)	1.401(8)
C(17)–C(18)	1.388(10)	C(25)–C(26)	1.378(9)
C(18)–C(19)	1.359(10)	C(26)–C(27)	1.390(9)
C(19)–C(20)	1.365(9)	C(27)–C(28)	1.376(9)
C(20)–C(21)	1.404(9)	C(28)–C(29)	1.384(9)
C(21)–C(32)	1.406(9)	C(29)–C(24)	1.403(8)
C(21)–C(22)	1.466(8)	C(29)–C(30)	1.491(9)
C(22)–C(23)	1.390(9)	C(30)–C(31)	1.323(10)
C(23)–C(24)	1.485(9)	C(31)–C(32)	1.457(9)
C(31)–C(32)–C(17)	118.0(6)	C(23)–C(24)–C(25)	117.4(5)
C(21)–C(32)–C(17)	118.5(6)	C(29)–C(24)–C(25)	118.7(5)
C(32)–C(17)–C(18)	121.7(6)	C(24)–C(25)–C(26)	121.2(6)
C(17)–C(18)–C(19)	119.7(6)	C(25)–C(26)–C(27)	119.6(6)
C(18)–C(19)–C(20)	120.3(7)	C(26)–C(27)–C(28)	119.6(6)
C(19)–C(20)–C(21)	121.6(6)	C(27)–C(28)–C(29)	121.7(6)
C(20)–C(21)–C(32)	116.8(5)	C(28)–C(29)–C(24)	119.2(6)
C(20)–C(21)–C(22)	118.7(5)	C(28)–C(29)–C(30)	118.0(5)
C(32)–C(21)–C(22)	124.5(5)	C(24)–C(29)–C(30)	122.7(5)
C(21)–C(22)–C(23)	128.1(6)	C(29)–C(30)–C(31)	125.3(5)
C(22)–C(23)–C(24)	126.4(5)	C(30)–C(31)–C(32)	128.5(6)
C(23)–C(24)–C(29)	124.0(5)	C(31)–C(32)–C(21)	123.3(5)
C(21)–C(22)–C(23)–C(24)	−0.3(9)	C(29)–C(30)–C(31)–C(32)	−5.1(10)
C(22)–C(23)–C(24)–C(29)	−56.4(8)	C(30)–C(31)–C(32)–C(21)	−60.8(9)
C(23)–C(24)–C(29)–C(30)	−3.7(8)	C(31)–C(32)–C(21)–C(22)	5.5(10)
C(24)–C(29)–C(30)–C(31)	66.3(8)	C(32)–C(21)–C(22)–C(23)	55.1(9)

[a] Roman numeral I as superscript denotes the symmetry transformation $-x$, $1-y$, $1-z$. [b] π_1, π_2, π_3, and π_4 denote the mid-points of the C(6)–C(7), C(14)–C(15), C(22)–C(23), and C(30)–C(31) double bonds, respectively.

labelling scheme of Fig. 1. * Bond distances, bond angles, and selected torsion angles are given in Table 3, and least-squares planes through sets of atoms in Table 4. Tables of hydrogen atom coordinates and structure factors are available from the first author upon request.

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* The molecular center is located at (0, 1/2, 1/2), namely Wyckoff position 1(g); the other half of the tetrameric molecule can be generated from the atoms in the asymmetric unit by the symmetry transformation ($-x$, $1-y$, $1-z$).

TABLE 4

LEAST-SQUARE PLANES[a]

Plane	Atoms fitted	l	m	n	d	rms Δ (Å×10^4)
	(i) Cu_4Cl_4 ring					
1	Cu(1), Cl(1), Cu(2), Cl(2)	0.0264	0.9868	0.1598	5.3273	1060
2	Cu(1), Cl(2), $Cu(1)^I$, $Cl(2)^I$	−0.0205	−0.5205	0.8536	0	0
	(ii) DBCOT A					
3	C(1), C(2), C(3), C(4), C(5), C(16)	−0.1205	0.9190	0.3755	5.1871	149
4	C(5), C(6), C(15), C(16)	−0.0842	0.9196	0.3838	5.3517	111
5	C(6), C(7), C(14), C(15)	−0.2835	0.8906	−0.3557	−0.3659	13
6	C(7), C(8), C(13), C(14)	−0.3133	0.3418	−0.8860	−4.9014	20
7	C(8), C(9), C(10), C(11), C(12), C(13)	0.3110	−0.3524	0.8827	4.8536	138
8	C(5), C(6), C(7), C(8)	0.4979	0.7492	−0.4368	−0.5373	23
9	C(5), C(8), C(13), C(16)	−0.2934	0.8892	−0.3511	−1.2401	64
10	C(13), C(14), C(15), C(16)	−0.8817	0.4694	−0.0476	−2.1470	15
	(iii) DBCOT B					
11	C(17), C(18), C(19), C(20), C(21), C(32)	−0.0339	0.2275	0.9732	3.7981	46
12	C(21), C(22), C(31), C(32)	−0.1137	0.2550	0.9602	4.1592	172
13	C(22), C(23), C(30), C(31)	0.5676	0.3203	0.7584	1.9854	153
14	C(23), C(24), C(29), C(30)	0.9760	0.1810	0.1211	−0.5800	120
15	C(24), C(25), C(26), C(27), C(28), C(29)	0.9780	0.1497	0.1455	−0.6520	111
16	C(21), C(22), C(23), C(24)	0.5236	−0.4390	0.7302	−1.8111	8
17	C(21), C(24), C(29), C(32)	0.5904	0.2930	0.7521	0.9781	88
18	C(29), C(30), C(31), C(32)	0.2827	0.9116	0.2986	2.3827	146

Angles between planes[b]

		Type α_a	Type α_c	Type β
Cu_4Cl_4 ring	1–2, 112.2°	–	–	–
DBCOT A	–	4–5, 45.1°; 5–6, 44.9°	8–9, 47.7°; 9–10, 46.1°	3–4, 2.1°; 6–7, 0.6°
DBCOT B	–	12–13, 41.8°; 13–14, 45.3°	16–17, 43.1°; 17–18, 48.8°	11–12, 4.9°; 14–15, 2.9°

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[a] Plane equation is of the form $lX_0 + mY_0 + nZ_0 = d$, where X_0, Y_0, Z_0 are orthogonal coordinates in Å referred to axes $\mathbf{a}_0$, $\mathbf{b}_0$, $\mathbf{c}_0$ respectively, with $\mathbf{a}_0$ parallel to $\mathbf{a}^\star$, $\mathbf{b}_0$ to $\mathbf{c} \times \mathbf{a}^\star$, and $\mathbf{c}_0$ to $\mathbf{c}$. [b] For definition of fold angle α and tilt angle β in benzannelated cyclooctatetraenes, see ref. 30.

Results and discussion

Labelling of the atoms in the asymmetric unit is given in Fig. 1. The crystal structure of **1** is composed of discrete tetrameric $[(C_{16}H_{12})CuCl]_4$ molecules mutually separated by normal Van der Waals contacts. Figure 2 shows a stereoscopic view of the structure along the *b* axis.

The Cu_4Cl_4 moiety takes the form of a centrosymmetric ring of alternating copper(I) and chloride ions. This "step" configuration (structure IV) is defined by three four-membered systems: Cu(1), Cl(1), Cu(2) and Cl(2) [plane 1 in Table 4]; Cu(1), Cl(2), $Cu(1)^I$ and $Cl(2)^I$, which are required by symmetry to be strictly coplanar [plane 2 in Table 4]; and $Cu(1)^I$, $Cl(1)^I$, $Cu(2)^I$ and $Cl(2)^I$ [related to plane 1 by the inversion center at (0, 1/2, 1/2)]. Mean planes 1 and 2 make a dihedral angle of 112.2°. The atoms fitted to plane 1 are not precisely coplanar; the nonplanarity may be described in terms of the root-mean-square deviation of the atoms from their mean plane (rmsΔ = 0.106 Å in Table 4), or alternatively by the torsion angle of Cu(1)–Cl(1)–Cu(2)–Cl(2) 14.4(1)°. The bond angles at Cu(1) and Cl(1) within the ring are significantly smaller than those at Cu(2) and Cl(2), respectively (Table 3). The four copper atoms lie at the corners of a parallelogram with edges of Cu(1)... Cu(2) = 3.439(1) Å and Cu(1)... $Cu(2)^I$ = 3.805(1) Å, which are far too long for any significant metal–metal interaction. The Cu–Cl bonds, which alternate around the ring, lie in the range 2.263(2)–2.278(2) Å, and the Cu(1)... Cl(2) separation is 3.464(2) Å. The "step" Cu_4Cl_4 ring of **1** (structure IV) is thus geometrically similar to, but topologically distinct from, the well-established "step" M_4X_4 skeleton found in several tetrameric (pnicogen ligand)–(coinage metal)–halogen cluster systems [4,6,25–27] (structure II), which contains both doubly and triply bridging halides and hence metal ions of variable coordination numbers.

The topologically equivalent but conformationally different "tub" ring (structure III) as found in $[(\text{norbornadiene})CuCl]_4$, **2**, [7] has crystallographically dictated $\bar{4}$ symmetry. None of its three four-membered sets of atoms are required to be precisely coplanar, and the dihedral angle between adjacent mean planes is 100.8°.

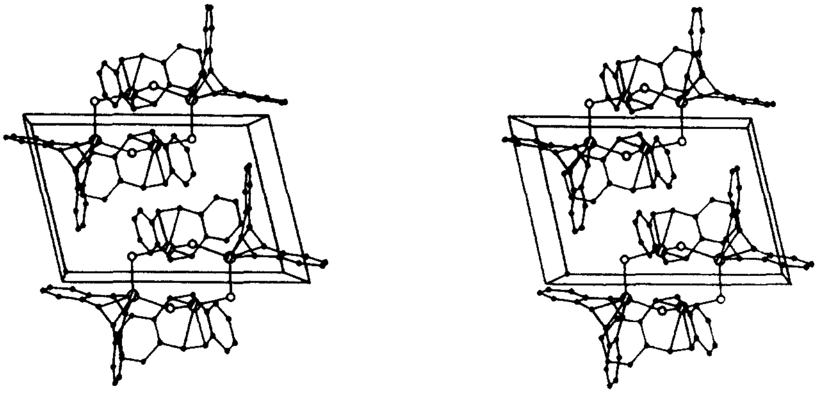

Fig. 2. Stereodrawing showing the molecular structure and packing arrangement in **1**. The origin of the unit cell lies at the lower left corner, with *a* pointing upwards, *b* towards the reader, and *c* from left to right.

Other geometrical parameters for this "tub" Cu_4Cl_4 ring are: Cu–Cl 2.275, Cu–Cl′ 2.296, Cu...Cl″ 3.091 Å, Cl–Cu–Cl′ 104.4, and Cu–Cl–Cu″ 94.1°. A common feature shared by the two Cu_4Cl_4 ring conformations III and IV is that bonding of each Cu atom to its adjacent Cl atoms is markedly asymmetric. Comparison of corresponding dimensions of the "step" ring in **1** and the "tub" ring in **2** shows that the former has shorter Cu–Cl bonds and larger values for the dihedral angles and bond angles. However, the most notable difference between the two structures is that, in the former, the organic ligand bonds to the metal in a bidentate mode.

The symmetry-independent Cu(1) and Cu(2) atoms in **1** are each coordinated, pincer-like and asymmetrically, by a pair of olefinic π-bonds of a dibenzo[*a,e*]cyclooctatetraene ligand. Their coordination environments (Table 3) are reminiscent of that around the Cu atom in $[(1,5\text{-cyclooctadiene})CuCl]_2$ [9] but differ from it in significant aspects. The metal coordination in the centrosymmetric dimer has been described as "quasi-tetrahedral" with two pairs of nearly equal Cu–Cl bonds (2.288 and 2.299 Å) and Cu-π (where π signifies the center of an olefinic ligand) bonds (2.05 and 2.22 Å). In **1** however, each Cu atom is bonded asymmetrically to surrounding ligands of the same type; furthermore, the two Cu–Cl bonds and the stronger Cu-π bond constitute a trigonal planar arrangement (Table 4) characteristic of that found in **2** [7] and $[(\text{cyclooctatetraene})CuCl]_n$, **4** [10]. Unlike the case in **2**, the Cu atoms in **1** and **4** each has an additional olefinic ligand * at a distance of 2.5–2.7 Å, so that the metal coordination may be termed distorted trigonal pyramidal. The structural relationship between these two cyclooctatetraene complexes of copper(I) chloride can be seen in the following light. The structure of **4** consists of continuous chains of alternating Cu and Cl atoms with two non-adjacent double bonds of a cyclooctatetraene moiety bound asymmetrically to each metal center. Replacement of the cyclic polyolefin by its *sym*-dibenzannelated derivative, as in **1**, leads to the formation of cyclic Cu_4Cl_4 "step" rings with retention of the "pincer" mode of cyclic polyolefin-metal bonding.

The two dibenzo[*a,e*]cyclooctatetraene ligands do not partake in metal-aromatic bonding interactions of the types found in $C_6H_6 \cdot CuAlCl_4$ [28] and benzocyclooctatetraene · $AgClO_4$ [1]. Both organic ligands have dimensions comparable to those of the uncomplexed molecule [29,30], except for significant lengthening of the C(6)–C(7) and C(22)–C(23) double bonds which are closely bound to Cu(1) and Cu(2), respectively. The conformation of the central eight-membered ring in ligand **A** is more folded, while that of ligand **B** is considerably more distorted, with respect to that of the free molecule (mean torsion angle about C–C single bonds 59.7° [29], α_a 43.2°, α_c 46.3°, and β 2.9° [30]); this may be seen from the torsion angles in Table 3, or the fold angles α and tilt angles β in Table 4.

Ring structures III and IV should be included in a survey of known stereochemistries for various $L_m(MX)_n$ stoichiometries [31], and it remains an open question as to whether the M_4X_4 core can exist in the "cubane-like", "tub", and "step" configurations in combination with π-olefinic ligands, and/or in the "tub" configuration with less bulky pnicogen ligands. Further studies on tetrameric bromide and iodide bridged coinage metal π-complexes of cyclooctatetraene and its benzanne-

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* This second double bond in the same cyclooctatetraene molecule was not considered to interact significantly with the copper atom in **4** and the metal coordination was described as distorted trigonal planar [10].

lated derivatives may be expected to provide some answers and interesting results in this regard.

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