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A novel one-dimensional polymeric complex of a tetraaza-macrocycle–copper(II) unit with a $[Cu(C_2O_4)_2(CH_3CN)]^{2-}$ bridging anion

Yanping Li,[a]* Pin Yang,[a] Zixiang Huang[b] and Fuxin Xie[c]

[a]Institute of Molecular Science, Chemical Biology and Molecular Engineering Laboratory of Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic China, [b]Fujian Institute of Research on The Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic China, and [c]Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic China

Correspondence e-mail: yangpin@sxu.edu.cn

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Key indicators

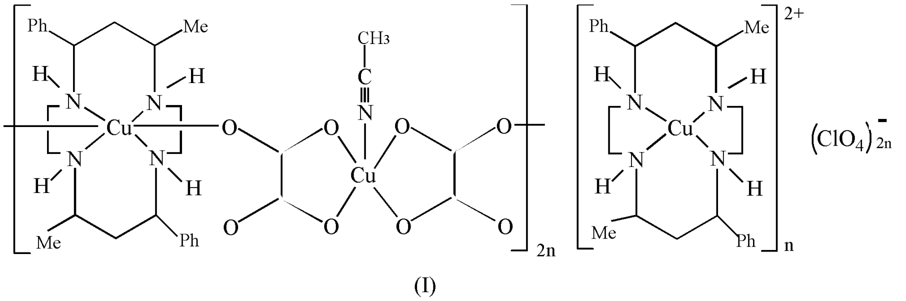
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.064
wR factor = 0.174
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, *catena*-poly[(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradecane)copper(II) bis[[(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradecane)copper(II)]-μ-oxalato-[(acetonitrile)copper(II)]-μ-oxalato] diperchlorate], $[Cu(C_{24}N_4H_{36})][Cu_4(C_2O_4)_4(C_{24}N_4H_{36})_2(CH_3CN)_2](ClO_4)_2$, the $\{(CuC_{24}N_4H_{36})\text{-}\mu\text{-}[Cu(C_2O_4)_2(CH_3CN)]\}_{2n}$ component is a one-dimensional chain polymeric complex of copper(II) bridged by $[Cu(C_2O_4)_2(CH_3CN)]^{2-}$. In the structure, there are three types of copper(II) coordination environment. The coordination environment around the Cu^{II} atom in $(CuL)^{2+}$ of the polymer (L is 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradecane) is an elongated octahedron, the Cu^{II} atom in $[Cu(C_2O_4)_2(CH_3CN)]^{2-}$ exhibits a square-based pyramidal geometry, while the Cu^{II} atom in the $(CuL)^{2+}$ counter-cation exhibits a square-planar geometry. The Cu atoms coordinated by L lie on inversion centers. The Cu$\cdots$Cu distances are 6.092 (4) and 5.551 (4) Å.

Comment

The current surge of research activity in the area of coordination polymers has been motivated by the ability of metal-ligand coordination to provide a facile approach to the controlled assembly of one-, two- or three-dimensional extended networks. The crystal engineering of coordination polymers with inner cavities or channels of desired size has been achieved recently by using suitable bidentate ligands (Jung *et al.*, 1998; Blake *et al.*, 1997; Yaghi *et al.*, 1998). This is of considerable interest for potential applications of these materials as catalysts, molecular sieves and ion exchangers (Ferlay *et al.*, 1999). As part of our interest in this area, we have designed and synthesized a new one-dimensional chain polymeric complex of copper(II), (I).



(I)

Some features of the molecular geometry of (I) are listed in Table 1 and shown in Figs. 1 and 2. The crystal structure of (I) is built of polymeric neutral $[(CuL)\text{-}\mu\text{-}[Cu(C_2O_4)_2(CH_3CN)]]$ molecules (L is 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradecane), co-crystallized $(CuL)^{2+}$ cations and

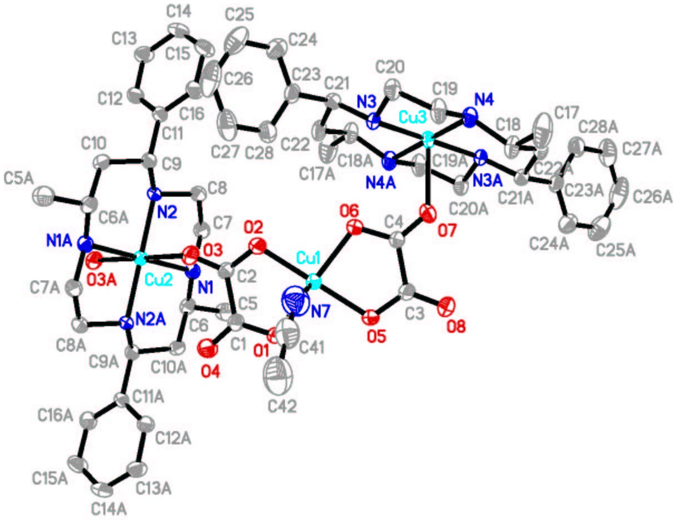


Figure 1
The structure of the neutral polymer chain of the title compound shown with 30% probability ellipsoids. H atoms have been omitted and atoms labeled with the suffix 'A' are related by the symmetry code ($1 - x, 1 - y, -z$). The $(\mathrm{Cu}4L)^{2+}$ cation and perchlorate anions have been omitted for clarity.

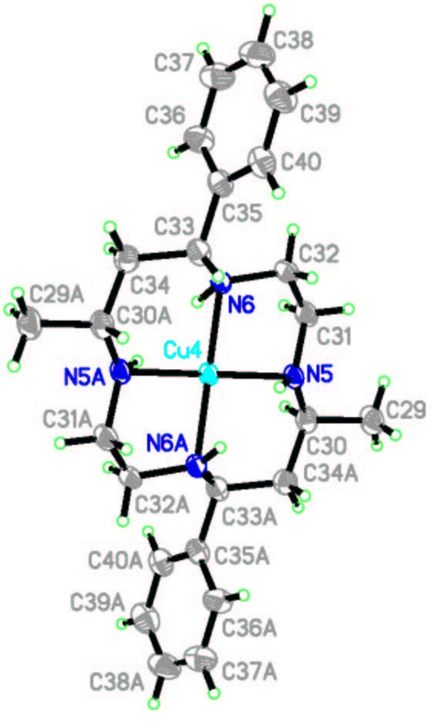


Figure 2
The structure of the $(\mathrm{Cu}4L)^{2+}$ cation. Atoms labeled with the suffix 'A' are related by the symmetry code ($-1 - x, -y, 1 - z$).

perchlorate anions. In this complex, there are three types of copper(II) coordination environment. The coordination environment around the Cu$^{\mathrm{II}}$ atom in the $(\mathrm{Cu}L)^{2+}$ moiety of the polymer chain is an elongated octahedron with short bonds formed by the N atoms from ligand L [Cu—N = 2.029 (5)–2.065 (4) Å]. The axial coordination sites are occupied by two oxalate O atoms from $[\mathrm{Cu(C_2O_4)_2(CH_3CN)}]^{2-}$ [Cu—O = 2.371 (4)–2.434 (4) Å]. The Cu$^{\mathrm{II}}$ atom lies at the center of the octahedron, on an inversion center. The two benzene rings of the ligand L are parallel. The Cu$^{\mathrm{II}}$ atom in $[\mathrm{Cu(C_2O_4)_2(CH_3CN)}]^{2-}$ exhibits a square-based pyramidal geometry whose basal plane is formed by four O atoms [Cu—O = 1.925 (4)–1.955 (4) Å] from the two oxalates. The apical site is occupied by the N atom from acetonitrile [Cu—N = 2.607 (10) Å]. The two units form a one-dimensional polymeric chain complex of copper(II). The unit $[\mathrm{Cu(C_2O_4)_2(CH_3CN)}]^{2-}$ acts as a bridging group. The chain is wave-like, with a C2—O3—Cu2 angle of 145.5 (4)° and a C4—O7—Cu3 angle of 134.0 (4)° (Fig. 3). The distances between Cu1 and Cu2, and between Cu1 and Cu3 are 6.092 (4) and 5.551 (4) Å, respectively. Atom Cu4 in the $(\mathrm{Cu}L)^{2+}$ cation lies on an inversion center and exhibits a square-planar geometry coordinated by four N atoms from the ligand L [Cu—N = 2.022 (5)–2.048 (4) Å] (Fig. 2). In the crystal structure, components are connected by C—H$\cdots$O hydrogen bonds (Table 2).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. The ligand L_0 (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradiene) was synthesized according to a literature method (Li, 1987). Anhydrous $\mathrm{K_2CO_3}$ (41.4 g, 0.3 mol) was added to a mixed solution of cyclohexane (150 ml) and ether (300 ml) containing benzoyl acetone (32.4 g, 0.2 mol) and ethylenediamine (12 g, 0.2 mol). The solution was stirred and refluxed for 5 h, then filtered. The filtrate was evaporated, and the residue was diffused with ether and refigerated overnight. The light yellow solid obtained was filtered off and washed with ether. Recrystallization of the solid from petroleum ether yielded white flaky crystals (yield 55%). The ligand L (5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetracyclotetradecane) was prepared by reducing L_0 (22.5 g, 0.06 mol) with $\mathrm{NaBH_4}$ (6.85 g, 0.18 mol) in methanol and was recrystallized from cyclohexane. L (1.9 g, 5 mmol) and $\mathrm{Cu(ClO_4)_2\cdot 6H_2O}$ (1.9 g, 5 mmol) were dissolved in methanol (75 ml), the solution was stirred and refluxed for 2 h. The red solid precipitate was filtered off and recrystallized from methanol to give red crystals of $\mathrm{Cu}L\mathrm{(ClO_4)_2}$. $\mathrm{Cu}L\mathrm{(ClO_4)_2}$ (0.64 g, 1 mmol) was dissolved in $\mathrm{CH_3CN}$ (30 ml). To this solution was added $\mathrm{(C_5H_{11}N)_2C_2O_4\cdot 2H_2O}$ (Julve & Khan, 1983) (0.29 g, 1 mmol) in $\mathrm{H_2O}$ (10 ml). The mixture was stirred to obtain a clear purple solution. Well-shaped purple crystals of the title complex were obtained from the above solution by slow evaporation at room temperature after three weeks. Elemental analyses for $\mathrm{C_{84}H_{114}Cl_2Cu_5N_{14}O_{24}}$ calculated: C 48.16, H 5.45, N,9.36%; found: C 48.05, H 5.66, N 9.64%.

Crystal data

$\mathrm{[Cu(C_{24}H_{36}N_4)][Cu_4(C_2O_4)_4\text{-}(C_{24}H_{36}N_4)_2(C_2H_3N)_2](ClO_4)_2}$
$M_r = 2092.54$
Triclinic, $P\bar{1}$
$a = 11.2419$ (5) Å
$b = 14.5966$ (7) Å
$c = 15.8730$ (8) Å
$\alpha = 64.8130$ (12)°
$\beta = 86.6890$ (12)°
$\gamma = 81.0760$ (12)°
$V = 2328.38$ (19) Å^3
$Z = 1$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5807 reflections
$\theta = 1.6$–25.1°
$\mu = 1.26$ mm^{-1}
$T = 293$ (2) K
Block, purple
0.60 × 0.44 × 0.20 mm

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Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.523$, $T_{\max} = 0.777$
11947 measured reflections
8044 independent reflections
6479 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25.1°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 16$
$l = -18 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.174$
$S = 1.01$
8044 reflections
587 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 10.7785P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.97$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O5	1.925 (4)	Cu4—N6	2.022 (5)
Cu1—O2	1.931 (4)	Cu4—N5	2.048 (4)
Cu1—O1	1.952 (4)	O1—C1	1.280 (6)
Cu1—O6	1.955 (4)	O2—C2	1.280 (7)
Cu2—N2	2.029 (4)	O3—C2	1.221 (6)
Cu2—N1	2.065 (4)	O4—C1	1.223 (7)
Cu2—O3	2.434 (4)	O5—C3	1.287 (7)
Cu3—N3	2.044 (4)	O6—C4	1.291 (7)
Cu3—N4	2.059 (4)	O7—C4	1.227 (7)
Cu3—O7	2.371 (4)	O8—C3	1.215 (7)
O5—Cu1—O2	174.2 (2)	N1—Cu2—O3	90.85 (16)
O5—Cu1—O1	93.82 (15)	N3—Cu3—N4	85.65 (18)
O2—Cu1—O1	84.99 (16)	N3—Cu3—O7	88.68 (17)
O5—Cu1—O6	84.96 (16)	N4—Cu3—O7	86.58 (18)
O2—Cu1—O6	95.06 (17)	N6—Cu4—N5	86.26 (18)
O1—Cu1—O6	168.5 (2)	C2—O3—Cu2	145.5 (4)
N2—Cu2—N1	86.28 (17)	C4—O7—Cu3	134.0 (4)
N2—Cu2—O3	88.38 (15)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C42—H42*C*$\cdots$O8$^{\rm i}$	0.96	2.43	3.369 (13)	166
C33—H33*A*$\cdots$O13	0.98	2.54	3.376 (12)	144

Symmetry code: (i) $-x, -y, 1 - z$.

H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^3—H = 0.96 or 0.97 Å and Csp^2—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) and 1.2$U_{\rm eq}$(C), respectively. H atoms attached to N atoms were placed in geometrically idealized positions, with Nsp^3—H = 0.86 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N).

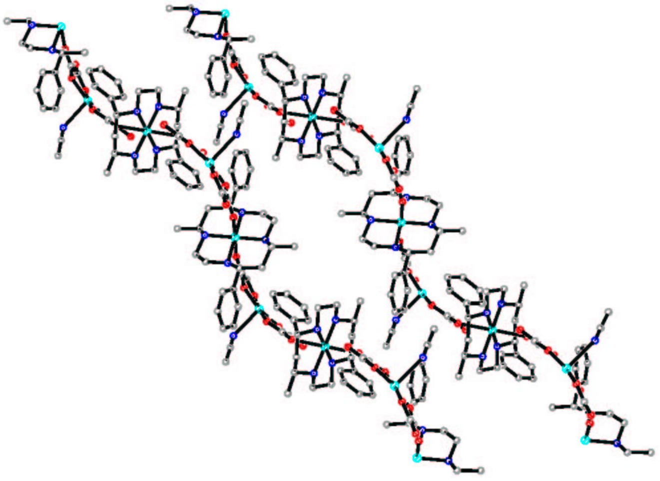

Figure 3
The wave-like chain of the [Cu*L*-Cu(ox)]$_{2n}$ component of the title structure. All H atoms have been omitted for clarity.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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