metal-organic compounds

Di-μ-chlorido-1:2κ²Cl,2:3κ²Cl-tetra-chlorido-1κCl,2κ²Cl,3κCl-bis[N,N″-bis(2-furylmethylene)diethylene-triamine]-1κ³N,N′,N″;3κ³N,N′,N″-tricopper(II)

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The complete title trinuclear Cu[II] complex, $[Cu_3Cl_6(C_{14}H_{16}N_3O_2)_2]$, is generated by twofold symmetry with one Cu atom lying on the rotation axis. The central Cu atom adopts a distorted tetrahedral $CuCl_4$ geometry. The terminal Cu atom is five-coordinated in a distorted square-pyramidal coordination environment consisting of three N atoms of the ligand, one bridging Cl atom and one terminal Cl atom. Intermolecular C—H···Cl hydrogen bonds help to establish the packing.

Related literature

For background, see: Erxleben et al. (2001); Mukherjee et al. (2002).
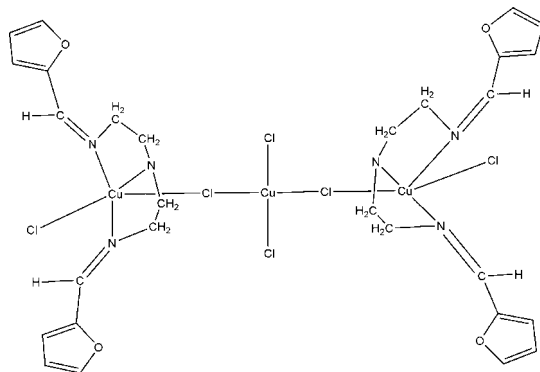
Experimental

Crystal data

$[Cu_3Cl_6(C_{14}H_{16}N_3O_2)_2]$	V = 1823.1 (4) Å³
M_r = 919.92	Z = 2
Monoclinic, $P2/n$	Mo $K\alpha$ radiation
a = 10.9456 (15) Å	μ = 2.22 mm⁻¹
b = 7.5287 (10) Å	T = 298 (2) K
c = 22.248 (2) Å	0.26 × 0.14 × 0.05 mm
β = 96.048 (2)°	

Data collection

Siemens SMART CCD diffractometer	8801 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3200 independent reflections
	1749 reflections with $I > 2\sigma(I)$
T_{min} = 0.597, T_{max} = 0.897	R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047	213 parameters
$wR(F^2)$ = 0.088	H-atom parameters constrained
S = 0.99	$\Delta\rho_{max}$ = 0.64 e Å⁻³
3200 reflections	$\Delta\rho_{min}$ = −0.42 e Å⁻³

Table 1
Selected bond lengths (Å).

Cu1—N3	1.988 (4)	Cu1—Cl2	2.9998 (16)
Cu1—N2	1.999 (4)	Cu2—Cl2	2.2379 (14)
Cu1—N1	2.011 (4)	Cu2—Cl3	2.2668 (16)
Cu1—Cl1	2.2489 (15)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···Cl3ⁱ	0.93	2.80	3.669 (7)	156
C10—H10···Cl3ⁱⁱ	0.93	2.80	3.451 (8)	128

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $-x, -y, -z + 1$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2633).

References

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Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
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Sheldrick, G. M. (1997b). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Di-*μ*-chlorido-1:2*κ*²*Cl*,2:3*κ*²*Cl*-tetrachlorido-1*κCl*,2*κ*²*Cl*,3*κCl*-bis[*N*,*N*''-bis(2-furylmethylene)diethylenetriamine]-1*κ*³*N*,*N*',*N*'';3*κ*³*N*,*N*',*N*''-tricopper(II)

Q. Wang, D.-Q. Wang and Y.-Y. Sun

Comment

Transition metals complexed with multidentate Schiff base ligands result in homo and/or heteronuclear metal complexes with insteresting stereochemistry (*e.g.* Erxleben *et al.*, 2001). Such species can be used as biological models, catalysis, and molecular ferromagnets (Mukherjee *et al.*, 2002). The Schiff base *N*,*N*'-bis(2-furylmethylene)diethylenetriamine is considered to be a good chelating ligand, which can coordinate to transition metals as a tridentate, tetradentate or pentadentate ligand, with consequent variable chemical properties. We report here the synthesis and crystal structure of the title compound, (I), a new copper(II) complex, with a multidentate Schiff base ligand derived from the condensation of 2-furaldehyde and diethylenetriamine.

The complete molecule of (I) (Fig. 1) is generated by 2-fold symmetry. The terminal Cu1 atom is five-coordinated in a distorted square-pyramidal coordination environment consisting of three N atoms of the ligand, one bridging Cl atom and one terminal Cl atom. Cu2 (site symmetry 2) is tetrahedrally coordinated by two bridging Cl atoms and two terminal Cl atoms (Table 1). The two five-membered rings Cu1—N1—C11—C12—N2 and Cu1—N2—C13—C14—N3 form a dihedral angle of 5.7 (3)°, and the dihedral angle between the mean planes of the furan rings is 25.7 (3) °. The Cu1···Cu2 separation is 4.6059 (9) Å.

In the crystal, intermolecular C—H···Cl hydrogen bonds lead to a three-dimensional network (Table 2).

Experimental

2-Furaldehyde (4 mmol, 384.4 mg) was added dropwise to a dichloromethane (20 ml) solution of diethylenetriamine (2 mmol, 206.4 mg). The mixture was heated under reflux with stirring for 1.5 h. An absolute ethanol solution (5 ml) of cupric chloride dihydrate (3 mmol, 511.4 mg) was then added dropwise, and the mixture was stirred at room temperature for another 15 h. The solution was filtered off, the filterate was kept at room temperature for about 12 days, after which large pale blue blocks of (I) were obtained.

Refinement

All H-atoms were positioned geometrically and refined using a riding model, with with C—H (methyne) 0.93, C—H = 0.97 (methylene), C—H 0.93 Å (aromatic) and U_{iso}(H) =1.2U_{eq}(C).
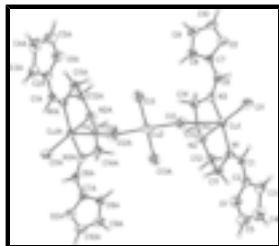
supplementary materials

Figures

Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the suffix A are generated by the symmetry operation ($-x + 1/2, y, -z + 3/2$). H atoms have been omitted for clarity.

Di-μ-chlorido-1:2κ^{2}Cl,2:3κ^{2}Cl-tetrachlorido-1κCl,2κ^{2}Cl,3κCl- bis[N,N''-bis(2-furylmethylene)diethylenetriamine]- 1κ^{3}N,N',N'';3κ^{3}N,N',N''-tricopper(II)

Crystal data

[Cu$_3$Cl$_6$(C$_{14}$H$_{16}$N$_3$O$_2$)$_2$]	F_{000} = 926
M_r = 919.92	D_x = 1.676 Mg m^{-3}
Monoclinic, $P2/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yac	Cell parameters from 1576 reflections
a = 10.9456 (15) Å	θ = 2.9–20.0º
b = 7.5287 (10) Å	μ = 2.22 mm^{-1}
c = 22.248 (2) Å	T = 298 (2) K
β = 96.048 (2)º	Block, pale blue
V = 1823.1 (4) Å^3	0.26 × 0.14 × 0.05 mm
Z = 2	

Data collection

Siemens SMART CCD diffractometer	3200 independent reflections
Radiation source: fine-focus sealed tube	1749 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.066
T = 298(2) K	θ_{max} = 25.0º
ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 13$
T_{min} = 0.597, T_{max} = 0.897	$k = -6 \rightarrow 8$
8801 measured reflections	$l = -21 \rightarrow 26$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.047	H-atom parameters constrained
$wR(F^2)$ = 0.088	$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2]$

where $P = (F_o{}^2 + 2F_c{}^2)/3$

$S = 0.99$	$(\Delta/\sigma)_{max} = 0.002$
3200 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
213 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C13	0.4074 (5)	−0.2812 (7)	0.6330 (2)	0.0646 (16)
H13A	0.3969	−0.3504	0.6689	0.077*
H13B	0.4537	−0.3517	0.6068	0.077*
Cu1	0.45072 (5)	0.05268 (9)	0.58051 (3)	0.0527 (2)
Cu2	0.2500	0.13781 (14)	0.7500	0.0624 (3)
Cl1	0.42526 (12)	0.2454 (2)	0.50298 (6)	0.0691 (5)
Cl2	0.32170 (13)	0.2627 (2)	0.66945 (6)	0.0689 (4)
Cl3	0.07882 (15)	−0.0122 (2)	0.71301 (7)	0.0956 (6)
C11	0.6627 (5)	0.0402 (8)	0.6707 (2)	0.0605 (16)
H11A	0.6451	0.0961	0.7082	0.073*
H11B	0.7511	0.0297	0.6711	0.073*
C7	0.1142 (5)	−0.1623 (8)	0.4910 (2)	0.0537 (15)
C2	0.7637 (5)	0.3940 (8)	0.6357 (3)	0.0523 (15)
O2	0.0691 (3)	−0.1249 (5)	0.43235 (18)	0.0719 (12)
O1	0.8276 (4)	0.3279 (6)	0.68845 (18)	0.0753 (12)
C6	0.2281 (5)	−0.0728 (7)	0.5094 (2)	0.0513 (14)
H6	0.2500	0.0148	0.4831	0.062*
C1	0.6602 (5)	0.2975 (8)	0.6072 (2)	0.0528 (15)
H1	0.6204	0.3552	0.5737	0.063*
C5	0.9170 (6)	0.4454 (11)	0.7032 (3)	0.086 (2)
H5	0.9746	0.4347	0.7369	0.104*
C14	0.2835 (5)	−0.2341 (7)	0.6005 (2)	0.0596 (15)
H14A	0.2462	−0.3378	0.5802	0.071*
H14B	0.2292	−0.1911	0.6291	0.071*
C3	0.8128 (5)	0.5445 (8)	0.6198 (2)	0.0615 (16)
H3	0.7868	0.6141	0.5864	0.074*

C8	0.0327 (5)	−0.2627 (8)	0.5169 (3)	0.0640 (16)
H8	0.0412	−0.3054	0.5564	0.077*
C9	−0.0679 (6)	−0.2912 (9)	0.4730 (3)	0.078 (2)
H9	−0.1392	−0.3544	0.4779	0.093*
C4	0.9142 (6)	0.5794 (10)	0.6643 (3)	0.085 (2)
H4	0.9673	0.6761	0.6657	0.101*
C10	−0.0405 (6)	−0.2098 (9)	0.4234 (3)	0.074 (2)
H10	−0.0904	−0.2108	0.3869	0.088*
N1	0.6121 (3)	0.1490 (6)	0.61850 (17)	0.0478 (11)
N3	0.3035 (4)	−0.0958 (6)	0.55647 (19)	0.0488 (12)
N2	0.4730 (4)	−0.1175 (6)	0.64975 (17)	0.0529 (12)
C12	0.6046 (5)	−0.1397 (8)	0.6653 (2)	0.0672 (17)
H12A	0.6392	−0.2077	0.6341	0.081*
H12B	0.6202	−0.2033	0.7032	0.081*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C13	0.077 (4)	0.051 (4)	0.066 (4)	0.003 (3)	0.006 (3)	0.012 (3)
Cu1	0.0446 (4)	0.0592 (5)	0.0538 (4)	−0.0022 (4)	0.0024 (3)	0.0115 (4)
Cu2	0.0607 (7)	0.0705 (8)	0.0559 (6)	0.000	0.0051 (5)	0.000
Cl1	0.0545 (9)	0.0818 (12)	0.0691 (10)	−0.0113 (8)	−0.0027 (7)	0.0301 (8)
Cl2	0.0692 (10)	0.0623 (11)	0.0764 (10)	−0.0040 (8)	0.0138 (8)	0.0099 (8)
Cl3	0.0959 (13)	0.1257 (18)	0.0656 (11)	−0.0453 (12)	0.0108 (9)	−0.0127 (10)
C11	0.055 (4)	0.067 (5)	0.057 (4)	0.002 (3)	−0.005 (3)	0.013 (3)
C7	0.050 (4)	0.056 (4)	0.054 (4)	0.007 (3)	−0.003 (3)	−0.011 (3)
C2	0.043 (3)	0.058 (5)	0.057 (4)	0.002 (3)	0.008 (3)	−0.003 (3)
O2	0.057 (3)	0.088 (3)	0.069 (3)	0.002 (2)	−0.003 (2)	−0.007 (2)
O1	0.066 (3)	0.083 (4)	0.075 (3)	−0.008 (3)	−0.003 (2)	−0.007 (2)
C6	0.050 (3)	0.050 (4)	0.056 (4)	0.005 (3)	0.014 (3)	−0.005 (3)
C1	0.045 (4)	0.065 (5)	0.049 (3)	0.015 (3)	0.010 (3)	0.002 (3)
C5	0.070 (5)	0.102 (7)	0.084 (5)	−0.019 (5)	−0.004 (4)	−0.020 (5)
C14	0.063 (4)	0.054 (4)	0.061 (4)	−0.009 (3)	0.005 (3)	0.000 (3)
C3	0.058 (4)	0.056 (4)	0.073 (4)	−0.001 (4)	0.014 (3)	0.002 (3)
C8	0.056 (4)	0.065 (5)	0.071 (4)	−0.012 (3)	0.008 (3)	−0.004 (3)
C9	0.052 (4)	0.066 (5)	0.115 (6)	−0.005 (3)	0.003 (4)	−0.017 (4)
C4	0.064 (4)	0.075 (6)	0.117 (6)	−0.029 (4)	0.023 (4)	−0.033 (5)
C10	0.051 (4)	0.078 (6)	0.087 (5)	0.011 (4)	−0.013 (4)	−0.033 (4)
N1	0.043 (3)	0.057 (3)	0.044 (3)	0.005 (2)	0.006 (2)	0.008 (2)
N3	0.049 (3)	0.048 (3)	0.052 (3)	−0.001 (2)	0.013 (2)	0.001 (2)
N2	0.053 (3)	0.048 (3)	0.055 (3)	−0.008 (2)	−0.009 (2)	0.009 (2)
C12	0.080 (5)	0.052 (5)	0.069 (4)	0.010 (4)	0.004 (3)	0.014 (3)

Geometric parameters (Å, °)

C13—N2	1.455 (6)	O2—C10	1.356 (6)
C13—C14	1.510 (6)	O1—C5	1.334 (7)
C13—H13A	0.9700	C6—N3	1.274 (5)
C13—H13B	0.9700	C6—H6	0.9300

Cu1—N3	1.988 (4)	C1—N1	1.273 (6)
Cu1—N2	1.999 (4)	C1—H1	0.9300
Cu1—N1	2.011 (4)	C5—C4	1.327 (8)
Cu1—Cl1	2.2489 (15)	C5—H5	0.9300
Cu1—Cl2	2.9998 (16)	C14—N3	1.462 (6)
Cu2—Cl2	2.2379 (14)	C14—H14A	0.9700
Cu2—Cl2ⁱ	2.2379 (14)	C14—H14B	0.9700
Cu2—Cl3	2.2668 (16)	C3—C4	1.432 (7)
Cu2—Cl3ⁱ	2.2668 (16)	C3—H3	0.9300
C11—N1	1.481 (6)	C8—C9	1.409 (7)
C11—C12	1.495 (7)	C8—H8	0.9300
C11—H11A	0.9700	C9—C10	1.324 (8)
C11—H11B	0.9700	C9—H9	0.9300
C7—C8	1.344 (7)	C4—H4	0.9300
C7—O2	1.376 (5)	C10—H10	0.9300
C7—C6	1.439 (7)	N2—C12	1.455 (6)
C2—C3	1.318 (7)	C12—H12A	0.9700
C2—O1	1.393 (6)	C12—H12B	0.9700
C2—C1	1.436 (7)		
N2—C13—C14	108.6 (4)	C2—C1—H1	113.6
N2—C13—H13A	110.0	C4—C5—O1	112.2 (6)
C14—C13—H13A	110.0	C4—C5—H5	123.9
N2—C13—H13B	110.0	O1—C5—H5	123.9
C14—C13—H13B	110.0	N3—C14—C13	107.3 (4)
H13A—C13—H13B	108.4	N3—C14—H14A	110.3
N3—Cu1—N2	82.91 (18)	C13—C14—H14A	110.3
N3—Cu1—N1	165.25 (18)	N3—C14—H14B	110.3
N2—Cu1—N1	82.92 (17)	C13—C14—H14B	110.3
N3—Cu1—Cl1	97.19 (13)	H14A—C14—H14B	108.5
N2—Cu1—Cl1	179.66 (14)	C2—C3—C4	106.3 (6)
N1—Cu1—Cl1	97.01 (13)	C2—C3—H3	126.9
N1—Cu1—Cl2	89.22 (12)	C4—C3—H3	126.9
N2—Cu1—Cl2	81.79 (13)	C7—C8—C9	107.1 (6)
N3—Cu1—Cl2	92.83 (13)	C7—C8—H8	126.4
Cl1—Cu1—Cl2	97.87 (5)	C9—C8—H8	126.4
Cl2—Cu2—Cl2ⁱ	130.30 (9)	C10—C9—C8	106.2 (6)
Cl2—Cu2—Cl3	105.36 (5)	C10—C9—H9	126.9
Cl2ⁱ—Cu2—Cl3	98.85 (6)	C8—C9—H9	126.9
Cl2—Cu2—Cl3ⁱ	98.85 (5)	C5—C4—C3	105.9 (6)
Cl2ⁱ—Cu2—Cl3ⁱ	105.36 (5)	C5—C4—H4	127.1
Cl3—Cu2—Cl3ⁱ	120.23 (11)	C3—C4—H4	127.1
N1—C11—C12	108.5 (4)	C9—C10—O2	111.7 (6)
N1—C11—H11A	110.0	C9—C10—H10	124.1
C12—C11—H11A	110.0	O2—C10—H10	124.1
N1—C11—H11B	110.0	C1—N1—C11	120.9 (5)
C12—C11—H11B	110.0	C1—N1—Cu1	126.7 (4)
H11A—C11—H11B	108.4	C11—N1—Cu1	111.7 (3)

C8—C7—O2	109.5 (5)	C6—N3—C14	121.2 (4)
C8—C7—C6	137.4 (6)	C6—N3—Cu1	125.5 (4)
O2—C7—C6	112.8 (5)	C14—N3—Cu1	113.2 (3)
C3—C2—O1	110.5 (5)	C12—N2—C13	114.4 (5)
C3—C2—C1	129.9 (6)	C12—N2—Cu1	107.1 (3)
O1—C2—C1	119.6 (5)	C13—N2—Cu1	109.2 (3)
C10—O2—C7	105.5 (5)	N2—C12—C11	108.5 (5)
C5—O1—C2	105.1 (5)	N2—C12—H12A	110.0
N3—C6—C7	129.5 (5)	C11—C12—H12A	110.0
N3—C6—H6	115.2	N2—C12—H12B	110.0
C7—C6—H6	115.2	C11—C12—H12B	110.0
N1—C1—C2	132.9 (5)	H12A—C12—H12B	108.4
N1—C1—H1	113.6		

Symmetry codes: (i) $-x+1/2, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯Cl3[ii]	0.93	2.80	3.669 (7)	156
C10—H10⋯Cl3[iii]	0.93	2.80	3.451 (8)	128

Symmetry codes: (ii) $x+1, y+1, z$; (iii) $-x, -y, -z+1$.

Fig. 1