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A heteroleptic tetranuclear copper amide/aryl complex: 1,4:2,3-bis(μ-2,4,6-trimethylphenyl-*C*,*C*)-1,2:3,4-bis[μ-bis(trimethylsilyl)amido-*N*,*N*]-tetracopper(I)

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The title compound [1,2:3,4-(CuBtsa)$_2$-1,4:2,3-(CuMes)$_2$] [Btsa is N(SiMe$_3$)$_2$; Mes is 2,4,6-Me$_3$C$_6$H$_2$] or [Cu$_4$(C$_9$H$_{11}$)$_2$-(C$_6$H$_{18}$NSi$_2$)$_2$], was obtained as the product of a ligand redistribution between the Ge^{II} amide, GeBtsa$_2$, and the Cu^I aryl, CuMes. It contains an almost planar eight-membered central ring, Cu$_4$C$_2$N$_2$, with two-coordinate Cu atoms (average Cu—C = 1.986 Å; average Cu—N = 1.936 Å; average C—Cu—N = 169.97°).

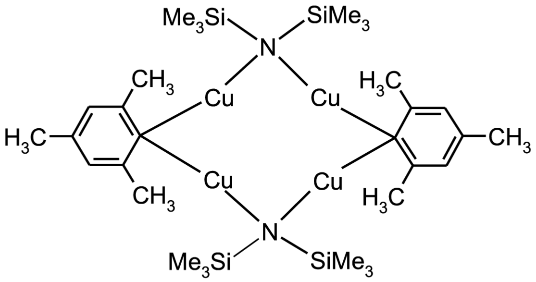
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.037
wR factor = 0.101
Data-to-parameter ratio = 19.7

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

Comment

The ligand transfer between copper aryls and bis(hypersilyl)tin or bis(hypersilyl)lead [hypersilyl = Hyp = tris(trimethylsilyl)silyl] has recently permitted the isolation of novel types of compounds (Klett *et al.*, 1999). Thus, the reaction of CuDmp (Dmp = 2,6-Mes$_2$C$_6$H$_3$) (Niemeyer, 1998) with SnHyp$_2$ yields the unusual Cu^I–stannylene complex HypCu–Sn(Dmp)Hyp. In contrast, the ligand exchange with PbHyp$_2$ affords base-free CuHyp, which is trimeric in the solid state, and the heteroleptic plumbylene Pb(Dmp)Hyp. As a continuation of this work, the reaction between the Ge^{II} amide, GeBtsa$_2$, and the Cu^I aryl, CuMes, has now been studied. It has been shown that this reaction produces colorless crystals of the title complex, (I), in moderate yield.



(I)

The molecular structure of (I) shows a tetranuclear copper aggregate (Fig. 1) which belongs to the frequently observed planar complexes of the Cu$_4$(μ-X)$_4$ type (Holloway & Melnik, 1995). The two-coordinate Cu atoms are bridged by C (C11 and C21) or N atoms (N1 and N2) of alternating mesityl and bis(trimethylsilyl)amide groups. The almost planar eight-membered Cu$_4$C$_2$N$_2$ ring is slightly puckered with C11 and C21 above [+0.231 (3) and +0.208 (3) Å] and N1 and N2 below [−0.138 (2) and −0.127 (2) Å] the plane defined by the four Cu atoms. The mesityl groups and the Btsa ligands, as defined by their NSi$_2$ fragments, are nearly perpendicular to this central Cu$_4$ plane, the interplanar angles being 83.05 (7) (C11–C16 plane), 86.61 (7) (C21–C26 plane), 83.60 (5) (N1/Si11/

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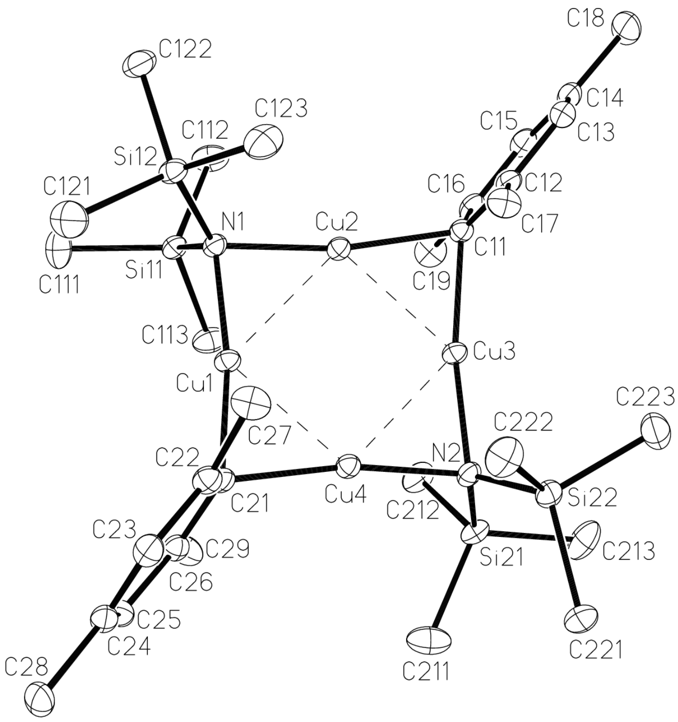

Figure 1
Displacement ellipsoid plot (at the 30% probability level) of (I). H atoms have been omitted for clarity.

Si12 plane) and 89.88 (4)° (N2/Si21/Si22 plane). As can be seen by the minor variations of the Cu—C (1.980–1.998 Å) and Cu—N distances (1.935–1.937 Å), a rather symmetric bonding situation, consistent with the presence of Cu—C—Cu and Cu—N—Cu *2e*–*3c* bonds, is observed within the $Cu_4C_2N_2$ ring. There are two different sets of Cu···Cu separations, which are of the same magnitude as previously observed for other oligo-nuclear copper compounds. Thus, shorter Cu1···Cu4 and Cu2···Cu3 distances (average 2.4307 Å) between C-bridged Cu atoms alternate with longer Cu1···Cu2 and Cu3···Cu4 separations (average 2.6111 Å) between N-bridged Cu atoms. It is interesting to compare these distances together with the angles at the ring atoms (average C—Cu—N = 169.97°, average Cu—C—Cu = 75.46°, average Cu—N—Cu = 84.84°) with the corresponding values in the homoleptic compounds [(CuMes)$_4$] (Eriksson & Håkansson, 1997) and [{CuN(SiMe$_3$)$_2$}$_4$] (James *et al.*, 1998), which are 1.993 Å (average Cu—C), 2.423 Å (average Cu···Cu), 164.9° (average C—Cu—C) and 74.9° (average Cu—C—Cu) for the former and 1.921 Å (average Cu—N), 2.6863 Å (average Cu···Cu), 178.7° (average N—Cu—N) and 88.8° (average Cu—N—Cu) for the latter, respectively.

Experimental

Under an atmosphere of purified argon, a solution of GeBtsa$_2$ (0,82 g, 2.08 mmol) in 10 ml of *n*-hexane was added at 273 K to CuMes (0.38 g, 2.08 mmol) in 20 ml of toluene. Stirring of the resulting orange–brown solution was continued for 2 h, whereupon all volatile materials were removed under reduced pressure. The remaining solid was extracted with *ca* 5 ml of *n*-hexane and the mixture was filtered over a glass filter frit. Cooling in a 278 K freezer afforded colorless crystals of (I) in 42% yield. Crystals gradually deepen in color above 418 K and decompose to a black liquid at 465–467 K. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.42 (*s*, 18H, SiMe$_3$), 2.08 (*s*, 3H, *p*-CH$_3$), 2.27 (*s*, 6H, *o*-CH$_3$), 6.66 p.p.m. (*s*, 2H, m-Mes). In addition, two weaker sets of signals (0.56, 1.99, 2.85, 6.77 and 0.35, 2.02, 2.94, 6.80 p.p.m.) are observed, which are not identical with the chemical shifts of the homoleptic compounds. They indicate the presence of other [(CuBtsa)$_x$(CuMes)$_y$] species in solution.

Crystal data

$[Cu_4(C_9H_{11})_2(C_6H_{18}NSi_2)_2]$
$M_r = 813.30$
Triclinic, $P\overline{1}$
$a = 9.171$ (2) Å
$b = 11.353$ (2) Å
$c = 20.314$ (4) Å
$\alpha = 101.98$ (1)°
$\beta = 94.56$ (2)°
$\gamma = 107.28$ (2)°
$V = 1952.9$ (7) Å^3

$Z = 2$
$D_x = 1.383$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta = 10.3$–12.2°
$\mu = 2.29$ mm^{-1}
$T = 173$ (2) K
Block, colorless
0.60 × 0.45 × 0.30 mm

Data collection

Rebuilt Syntex $P2_1$/Siemens $P3$ four-circle diffractometer
Wyckoff scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.423$, $T_{max} = 0.602$
9068 measured reflections
8527 independent reflections
7199 reflections with $I > 2\sigma(I)$

$R_{int} = 0.025$
$\theta_{max} = 27.0°$
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 13$
$l = -25 \rightarrow 25$
2 standard reflections every 198 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.101$
$S = 1.07$
8527 reflections
433 parameters
Only H-atom U's refined

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 1.1813P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.935 (2)	Cu1···Cu4	2.4291 (6)
Cu1—C21	1.982 (3)	Cu1···Cu2	2.6071 (9)
Cu2—N1	1.935 (2)	Cu2···Cu3	2.4322 (6)
Cu2—C11	1.984 (3)	Cu3···Cu4	2.6150 (9)
Cu3—N2	1.936 (2)	N1—Si12	1.750 (2)
Cu3—C11	1.980 (3)	N1—Si11	1.751 (2)
Cu4—N2	1.937 (2)	N2—Si21	1.746 (2)
Cu4—C21	1.998 (3)	N2—Si22	1.759 (2)
N1—Cu1—C21	169.86 (10)	Cu1—N1—Cu2	84.72 (9)
N1—Cu2—C11	169.86 (10)	Si21—N2—Si22	119.80 (13)
N2—Cu3—C11	170.15 (10)	Cu3—N2—Cu4	84.95 (9)
N2—Cu4—C21	170.01 (10)	Cu3—C11—Cu2	75.69 (10)
Si12—N1—Si11	121.38 (13)	Cu1—C21—Cu4	75.23 (10)

The H atoms were positioned with idealized geometry and refined in a riding model approximation, including free rotation for methyl groups. For most H atoms, the assigned U_{iso} was allowed to refine freely. Isotropic displacement parameters larger than 0.15 Å^2 were constrained to $1.5U_{eq}$ of the parent atom.

Data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*

(Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

References

Eriksson, H. & Håkansson, M. (1997). *Organometallics*, **16**, 4243–4244.

Holloway, C. E. & Melnik, M. (1995). *Rev. Inorg. Chem.* **15**, 147–386.

James, A. M., Laxman, R. K., Fronczek, F. R. & Maverick, A. W. (1998). *Inorg. Chem.* **37**, 3785–3791.

Klett, J., Klinkhammer, K. W. & Niemeyer, M. (1999). *Chem. Eur. J.* pp. 2531–2536.

Niemeyer, M. (1998). *Organometallics*, **17**, 4649–4656.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1989). *P*3 and *XDISK*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.