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Bis(μ_6-*cis*-2,4,6,8,10,12,14,16-octamethylcyclooctasiloxane-2,4,6,8,10,12,14,16-octolato)octakis[(dimethylformamide)copper(II)] dimethylformamide solvate enclosing a pyrazine molecule

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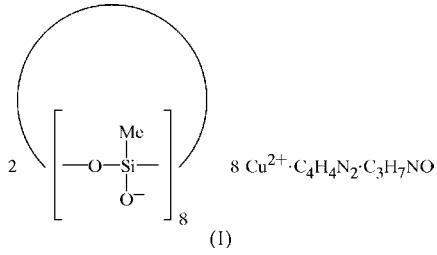
The title compound, $[Cu_8(C_8H_{24}O_2Si)_2(C_3H_7NO)_8]\cdot C_4H_4N_2\cdot C_3H_7NO$, features a sandwich-like cage enclosing a pyrazine molecule, both situated on a centre of inversion. In addition, the crystal structure contains one dimethylformamide molecule which is disordered over a centre of inversion. The copper layer, containing eight atoms, is located between two siloxanolate fragments. The whole structure of Cu atoms and siloxanolate rings is distorted by the pyrazine molecule, leading to an oval form. As a result, the angles between the Cu atoms differ at the copper layer. The difference in the angles could lead to some deviations in the Cu–Cu exchange interactions within the copper ring, which is of interest for molecular magnetism.

Comment

In recent years, the synthesis of metallaorganosiloxane compounds has attracted much attention due to the molecular magnetism of these compounds. A series of new crystalline



(I)

copper-containing organosiloxanes has been synthesized and structurally characterized (Lindeman *et al.*, 1997; Zucchi *et al.*, 2000; Molodtsova *et al.*, 1998; Abbati *et al.*, 2003; Zucchi *et al.*, 1998). We report here the structure of the title novel polyhedral methylsiloxane complex, (I), containing eight Cu atoms, with an encapsulated molecule of pyrazine.

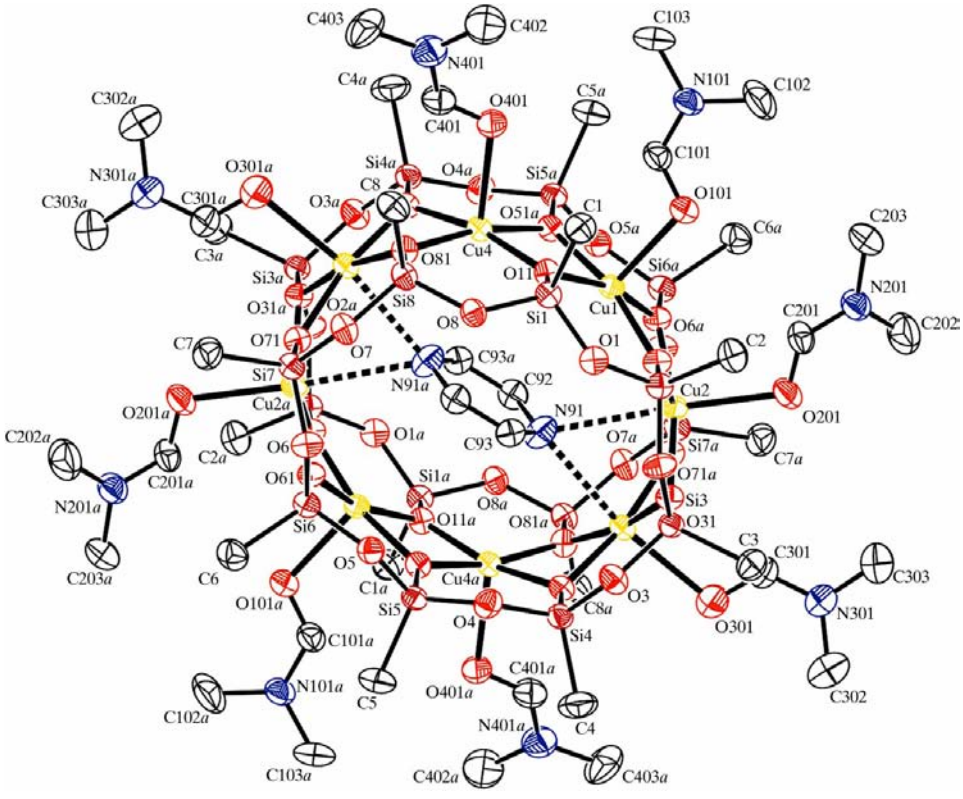


Figure 1
A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the disordered dimethylformamide molecule have been omitted for clarity. [Symmetry code: (*a*) $1-x, 1-y, 1-z$.]

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A perspective view of (I) is shown in Fig. 1. The compound features a cage enclosing a pyrazine molecule, both located on a centre of inversion. The cage is composed of two $\{[SiCH_3O]_8\}^{8-}$ rings which are connected by eight Cu atoms. The coordination of the Cu atoms by the O atoms can be described as quadratically pyramidal, where the plane is composed of O atoms of the $\{[SiCH_3O]_8\}^{8-}$ rings. The Cu atoms deviate only slightly from this plane, by 0.2594 (18), 0.2170 (17), 0.1940 (15) and 0.2241 (17) Å for atoms Cu1–Cu4, respectively. The Cu—O distances in the quadratic plane range from 1.934 (3) to 1.973 (3) Å. In addition, each Cu atom is further bonded to the O atom of one dimethylformamide molecule, with Cu—O distances ranging from 2.265 (4) to 2.428 (4) Å. All dimethylformamide molecules are oriented in the same way around the cage. The longest diagonal in the plane of the eight Cu atoms is the distance from Cu3 to its symmetry equivalent [7.9677 (12) Å]. The shortest diagonal (between Cu1 and the symmetry equivalent of Cu4) is 6.5288 (10) Å.

At the centre of the cage, there is a pyrazine molecule oriented almost in the direction of the longest diagonal. The N atoms of the pyrazine molecule show two short contacts to two Cu atoms [N91···Cu3 = 2.644 (4) Å and N91···Cu2 = 2.772 (5) Å]. The bonds of the O atoms connecting two Si atoms are significantly longer [1.630 (7) Å] than the Si—O bonds of the O atoms connecting an Si and a Cu atom [1.610 (7) Å]. The only exceptions to this are the bonds Si4—O3 [1.617 (4) Å] and Si4—O41 [1.622 (3) Å].

The eight-membered ring of Cu atoms shows Cu—Cu distances ranging from 2.8150 (9) (Cu2—Cu3) to 2.9587 (7) Å [Cu1—Cu4^{i}; symmetry code: (i) $1-x, 1-y, 1-z$]. The Cu—Cu—Cu angles at the Cu atoms which are bonded to the pyrazine molecule [131.93 (3)° for Cu2 and 128.69 (2)° for Cu3] are smaller than the remaining two [140.84 (3)° for Cu1 and 138.55 (3)° for Cu4].

In conclusion, it can be said that the title compound constitutes an ideal cage that has been designed to encapsulate a pyrazine guest molecule. The guest fits perfectly into the space offered by the host. Furthermore, attractive Cu···N interactions hold the guest tightly fixed in the cage.

Experimental

A three-necked flask was charged with EtOH (25 ml). NaOH (0.4 g, 0.01 mol) and $MeSi(OEt)_3$ (2.0 ml, 1.79 g, 0.01 mol) were added with vigorous stirring and the mixture was stirred for 1 h at room temperature. A solution of $CuCl_2$ (0.45 g, 0.003 mol) in EtOH (25 ml) was added dropwise, and then a mixture of water (1.08 g, 0.06 mol) and EtOH (5 ml) was quickly added. The reaction was heated for 20 min at a temperature slightly below boiling and then filtered hot through twice-folded filter paper. The resulting blue solution was evaporated using a rotory evaporator and dried in a vacuum (1 mm H g, 353 K). A bright-blue crystalline product was obtained (yield 1.68 g, 76.5%). This product was dissolved in dimethylformamide (15 ml) and the solution was added to a mixture of pyrazine (0.16 g) in dimethylformamide (15 ml). After a few months, green crystals of (I) were obtained which were suitable for X-ray diffraction analysis.

Crystal data

$[Cu_8(C_8H_{24}O_2Si)_2(C_3H_7NO)_8]\cdot C_4H_4N_2\cdot C_3H_7NO$
M_r = 2448.26
Monoclinic, $P2_1/n$
a = 16.9402 (16) Å
b = 18.6388 (18) Å
c = 17.2684 (16) Å
β = 110.679 (7)°
V = 5101.1 (9) Å^3
Z = 2
D_x = 1.594 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20012 reflections
θ = 3.5–25.8°
μ = 1.90 mm^{-1}
T = 173 (2) K
Block, light green
0.22 × 0.20 × 0.18 mm

Data collection

Stoe IPDS-II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.679, T_{max} = 0.726
39433 measured reflections
9372 independent reflections
5221 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 25.8°
$h = -20 \rightarrow 20$
$k = -22 \rightarrow 22$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.069
S = 0.74
9372 reflections
573 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0111P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

H atoms were placed in calculated positions and refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C)] using a riding model, with C—H = 0.95 and 0.98 Å for aromatic and methyl H atoms, respectively. The methyl groups of the non-disordered dimethylformamide molecules were allowed to rotate but not to tip.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3009). Services for accessing these data are described at the back of the journal.

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