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Hexakis(dimethylformamide)bis(hexaphenylcyclohexasiloxane) Dimethylformamide Solvate

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Hexakis(dimethylformamide)bis(hexaphenylcyclohexasiloxanehexaolato)-hexacopper(II) Dimethylformamide Solvate

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Abstract

The sandwich-like title complex, hexakis(dimethylformamide)- $1\kappa O, 2\kappa O, 3\kappa O, 4\kappa O, 5\kappa O, 6\kappa O$ -bis[2,4,6,8,10,12-hexaphenylsiloxane - 2, 4, 6, 8, 10, 12 - hexaolato (6^-) -

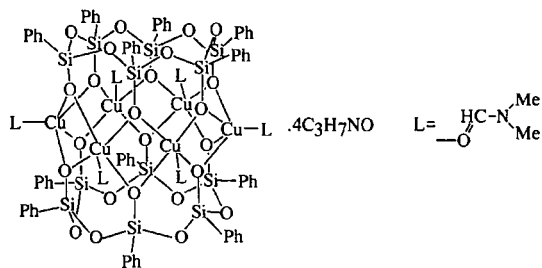
$1:2\kappa^2 O^1, 2:3\kappa^2 O^2, 3:4\kappa^2 O^3, 4:5\kappa^2 O^4, 5:6\kappa^2 O^5, 1:6\kappa^2 O^6$]-hexacopper(II) tetrakis(dimethylformamide) solvate, $[\text{Cu}_6(\text{C}_3\text{H}_7\text{NO})_6\{(\text{C}_6\text{H}_5)_6\text{O}_{12}\text{Si}_6\}_2]\cdot 4\text{C}_3\text{H}_7\text{NO}$, is comprised of two regular crown-shaped macrocyclic hexadentate organosiloxanolate ligands chelating a flat Cu_6 hexagon, as in the ethanol-solvated analogue investigated previously. The title complex has a more distorted shape than the trigonal ethanol-solvated analogue, being slightly side-oblated, but still contains a large empty inner channel accessible by small molecules (the diameter of the free cross-section being about 2.5 Å). Each Cu^{II} ion has a square-pyramidal coordination comprised of four basal siloxanolate O atoms and an apical dimethylformamide (DMFA) molecule (coordinated through its carbonyl group). The average bond lengths are $\text{Cu—O}(\text{Si})$ 1.964 (11) and $\text{Cu—O}(\text{DMFA})$ 2.215 (10) Å. The structure contains four additional DMFA molecules per complex unit, linked by weak $\text{C—H}\cdots\text{O}$ hydrogen bonds. Unexpectedly, the C=O bond length is longer [1.248 (10) and 1.255 (9) Å] in the uncoordinated DMFA molecules than in the coordinated molecules [1.214–1.227 (7) Å].

Comment

Recently, a new class of polynuclear metal complexes has been obtained (involving alkaline metals, Mn, Co, Ni and other bivalent transition metals, Cu and trivalent lanthanides) with polydentate regular macrocyclic organosiloxanolate $[-\text{RSi}(\text{O}^-)\text{O}-]_n$ ligands ($n = 6, 8$ or 12), which are known as polymetalloorganosiloxanates (PMOS) and have been structurally characterized by Struchkov & Lindeman (1995). The size and structure of the organocyclosiloxanolate ligands formed seem to be dependent mainly on the coordination characteristics (size, charge and coordination number) of the metal. The Cu^{II} complexes are of special interest since at least two quite different structural types have been obtained using different reaction conditions, *i.e.* sandwich-like complexes, such as $[\text{Cu}_6\{(\text{C}_6\text{H}_5)_6\text{O}_{12}\text{Si}_6\}(\text{EtOH})_6]$ [(1); Igonin *et al.*, 1992] or $\text{K}_2[\text{K}_2\text{Cu}_4\{(\text{C}_2\text{H}_5)_6\text{O}_{12}\text{Si}_6\}]\cdot 4n\text{-BuOH}$ [(2); Igonin *et al.*, 1993], and globular-like complexes, such as $[\text{Na}_4\text{Cu}_4\{(\text{C}_6\text{H}_5)_{12}\text{O}_{24}\text{Si}_{12}\}]\cdot 8n\text{-BuOH}$, (3), and $\text{K}_4[\text{Cu}_4(\text{O}_{24}\text{Si}_{12}\text{Vi}_{12})]\cdot 6n\text{-BuOH}$ [(4); Igonin *et al.*, 1991].

Complex (1) is rather unique as a result of its large empty inner channel and square-pyramidal coordination of the Cu atoms (by four siloxanolate groups and an axial solvent hydroxy group); other complexes have more compact structures and contain square-planar-coordinated Cu ions without the additional coordination by solvent molecules. To obtain additional evidence on the stability and reproducibility of such an open structure [in related PMOS compounds based on bivalent *d*-group metals or trivalent lanthanides, the central cavity is occupied by an additional small anion (Cl^- , OH^- or O^{2-}) (Struchkov & Lindeman, 1995)], a close ana-

logue of (1) has been synthesized, where the solvent coordinated is dimethylformamide (DMFA) instead of ethanol, [Cu₆{(C₆H₅)₆O₁₂Si₆}₂(DMFA)₆].4DMFA, (5), and its crystal structure is presented here.



The title complex, (5), has a sandwich-like structure (Fig. 1) very similar to that of complex (1). A central metal group comprises six Cu²⁺ ions arranged as a flat (within 0.001 Å) hexagon. In contrast to (1), however, with its high (trigonal) crystal symmetry, the hexagon

in complex (5) is slightly distorted; the distances between opposite Cu ions vary between 5.387 (1) and 5.986 (1) Å [5.614 Å in complex (1)]. The cation group coordinates two macrocyclic [–PhSi(O[–])O–]₆ phenylsiloxanolate hexa-anionic ligands. The ligands have an all-*cis* configuration with the olate groups directed towards the plane of the cations. Each ligand forms six six-membered chelate rings (–Cu–O–Si–O–Si–O–). These rings are not quite planar and have an approximate sofa conformation, with the Cu cation shifted out of a plane of the siloxane part of the ring. The shifts are most pronounced for the Cu1 and Cu3 atoms (0.41–0.47 Å), whereas the two symmetrically-independent chelate cycles containing the Cu2 atom are more planar (the shifts are 0.29 and 0.31 Å). The deviations of the Si and O atoms from the mean planes do not exceed 0.1 Å.

The Cu ions are shifted from the mean planes of the basal squares of the surrounding olate O atoms by 0.29 (for Cu2), 0.34 (Cu1) and 0.35 Å (Cu3) towards the external axially coordinated DMFA molecules [the Cu···O(DMFA) distances are 2.208–2.226 (1) Å].

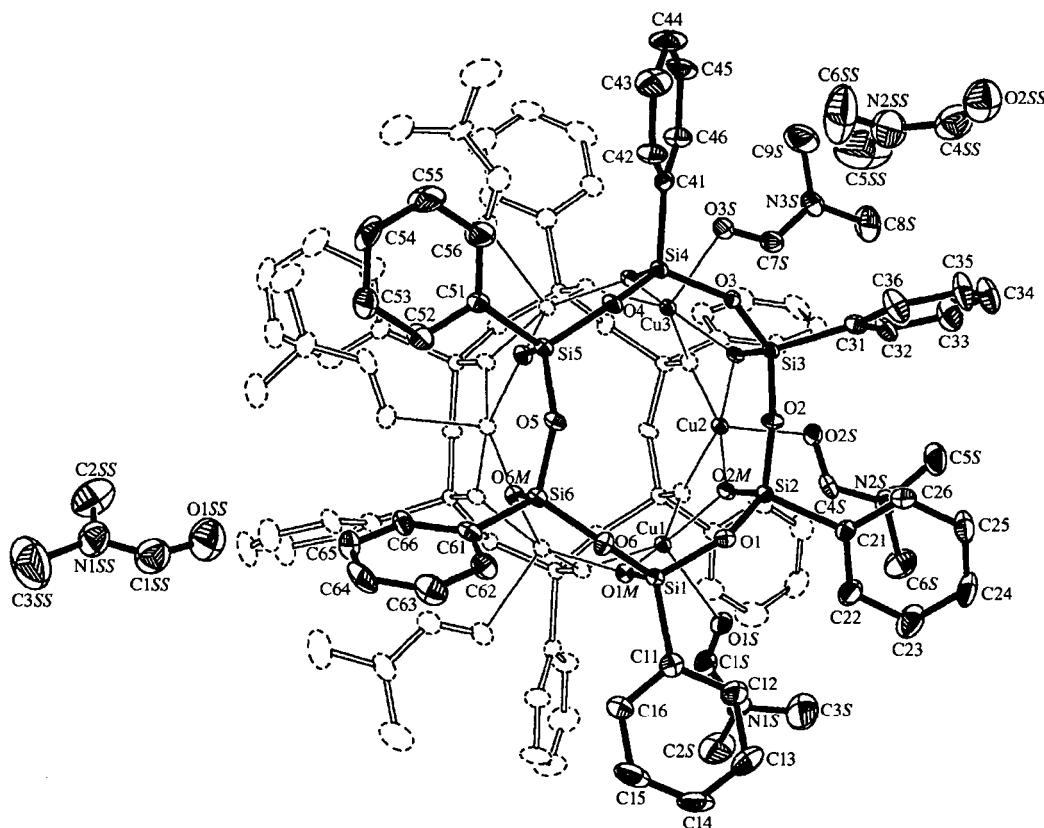


Fig. 1. Perspective view of complex (5) with the atomic labelling. The symmetrically-independent part of the complex (including two outer DMFA solvate molecules) is drawn with bold lines (covalent bonds; coordination bonds are shown as single lines). The symmetry-related part of the complex (*via* the centre of symmetry) is drawn as open bonds and dotted ellipsoids. Displacement ellipsoids are drawn at the 50% probability level.

These shifts are proportionate to the magnitude of the non-planarity of the corresponding chelate cycles and the general character of the distortions of the cationic hexagon in complex (5), which is flattened in approximately the Cu $\cdot\cdot$ ·Cu2' direction. In the close analogue (1), the shifts are 0.28–0.29 Å and axial ethanol ligands are loosely coordinated (Cu $\cdot\cdot$ ·O distances are 2.343 and 2.376 Å). It is possible that the better coordinating ability of DMFA compared with ethanol, rather than packing forces, destabilizes the ideal trigonal symmetry of the copper–siloxanolate framework.

The twelve-membered siloxane macrocycles have a slightly elliptical crown conformation, with Si atoms located 2.85–3.17 Å and O atoms 2.34–2.90 Å from the central axis of the ring. The Si—O—Si sections are nearly perpendicular to the mean plane of the Si atoms (dihedral angles 71.3–86.6°); the O2 and O5 'flaps' are tilted towards the centre of the ring, but the other four are tilted outwards and thus the lone electron pairs of the O atoms do not eclipse the central hole of the macrocycle, making it possible for small molecules or ions to enter the interior of the complex. The estimated diameter of the free channel is 1.7–2.7 Å on the level of the siloxane O atoms, 2.4–3.2 Å on the level of the olate O atoms and 2.6–3.2 Å on the level of the Cu atoms [using Bondi's (1964) van der Waals radii]. The Si—O bond lengths [1.624–1.641 (4) Å] and Si—O—Si angles (133.3–136.3°) have normal values (Dubchak, Shklover & Struchkov, 1983), the tetrahedral geometry of the Si atoms being only slightly distorted (Table 1).

Every olate group acts symmetrically, bridging two adjacent Cu ions. The Cu—O—Cu angles are close to 90° (Table 1) and the Si—O⁻ bonds are significantly shorter than the corresponding Si—O(Si) bonds in the hexasiloxane macrocycles (see above). The same difference between endo- and exocyclic Si—O bond lengths is observed in the unambiguously ionic structure of sodium triphenylcyclotrisiloxanolate (Dubchak, Shklover, Levitsky, Zhdanov & Struchkov, 1980) and in other PMOS (Struchkov & Lindeman, 1995). Also, the Cu—O bond lengths [1.947 (4)–1.978 (4) Å; Table 1] are close to the sums of the ionic radii of O²⁻ and Cu²⁺ [1.93 for four-coordinate copper and 2.01 Å for five-coordinate copper (Shannon & Prewitt, 1969; Shannon, 1976)]. This indicates that the interaction between the metal and siloxanolate ligands has mostly ionic character in complex (5) as well as in other PMOS.

The crystal structure of (5) contains four DMFA solvate molecules per PMOS unit. Their geometrical parameters agree well with those of coordinated DMFA molecules with the exception of an elongation of the C=O bond lengths in the uncoordinated molecules; 1.248 (10) and 1.255 (9) Å versus 1.214–1.227 (7) Å. This may be explained in part by these carbonyl groups participating in the formation of weak bifurcated C—H $\cdot\cdot$ ·O hydrogen bonds in the crystal [O1SS $\cdot\cdot$ ·H5SA—C5S(-x, 2 - y, 1 - z) with O $\cdot\cdot$ ·H 2.57 Å and O $\cdot\cdot$ ·H—C

146°; O1SS $\cdot\cdot$ ·H8SA—C8S(-x, 2 - y, 1 - z) with O $\cdot\cdot$ ·H 2.58 Å and O $\cdot\cdot$ ·H—C 123°; O2SS $\cdot\cdot$ ·H63A—C63(x + $\frac{1}{2}$, -y + $\frac{5}{2}$, z - $\frac{1}{2}$) with O $\cdot\cdot$ ·H 2.55 Å and O $\cdot\cdot$ ·H—C 172°; O2SS $\cdot\cdot$ ·H5SB—C5S(x - $\frac{1}{2}$, -y + $\frac{5}{2}$, z - $\frac{1}{2}$) with O $\cdot\cdot$ ·H 2.47 Å and O $\cdot\cdot$ ·H—C 173°].

Experimental

A mixture of polyphenylsiloxane (Andrianov & Zhdanov, 1957) (12.9 g, 0.1 mol) and NaOH (2 g, 0.05 mol) in butanol (250 ml) was refluxed with stirring until complete dissolution. Then 1.15 g (0.05 mol) of sodium was added at 343–353 K. The solution was heated to boiling and a solution of CuCl₂ (6.73 g, 0.05 mol) in butanol (80 ml) was introduced dropwise. The mixture was refluxed for 1–2 min, then NaCl was filtered off and blue crystals (3.4 g, yield 20%) were obtained on cooling to room temperature. Analyses: found for [Cu₆{(C₆H₅SiO₂)₆]₂(C₄H₉OH)₃(H₂O)₃] C 43.32, H 4.75, Si 14.63, Cu 15.78%; calculated for C₈₄H₉₆Cu₆O₃₀Si₁₂ C 43.78, H 4.20, Si 14.63, Cu 16.55%. Recrystallization from hot dimethylformamide gave crystals of (5) suitable for X-ray structure analysis [although very unstable in air (desolvating within a few seconds) and with poor reflecting ability].

Crystal data

[Cu₆(C₃₆H₃₀O₁₂Si₆)₂·
(C₃H₇NO)₆]₂·4C₃H₇NO
M_r = 2758.48
Monoclinic
P2₁/n
a = 17.750 (8) Å
b = 18.382 (10) Å
c = 20.129 (10) Å
β = 109.31°
V = 6198 (5) Å³
Z = 2
D_x = 1.478 Mg m⁻³
D_m not measured

Mo Kα radiation
λ = 0.71073 Å

Cell parameters from 24
reflections
θ = 8.1–9.5°
μ = 1.205 mm⁻¹
T = 153 (2) K
Prism
0.8 × 0.4 × 0.3 mm
Blue

Data collection

Siemens P3/PC diffractometer
ω/2θ scans
Absorption correction: none
10 103 measured reflections
9775 independent reflections
5450 reflections with
I > 2σ(I)

R_{int} = 0.0689
θ_{max} = 24.05°
h = -20 → 19
k = 0 → 21
l = -15 → 23
2 standard reflections
every 98 reflections
intensity decay: 3.6%

Refinement

Refinement on F²
R(F) = 0.0545
wR(F²) = 0.1195
S = 1.042
9763 reflections
749 parameters
H atoms refined as riding
w = 1/[σ²(F_o²) + (0.05P)²
+ 1.9P]
where P = (F_o² + 2F_c²)/3

(Δ/σ)_{max} = -0.406
Δρ_{max} = 0.548 e Å⁻³
Δρ_{min} = -0.473 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu1—O2M	1.948 (4)	Si3—O3	1.636 (4)	O6—Si1—O1—Si2	-114.5 (3)
Cu1—O5M ⁱ	1.964 (4)	Si3—C31	1.856 (6)	O2M—Si2—O2—Si3	-22.9 (4)
Cu1—O4M ⁱ	1.975 (4)	Si4—O4M	1.605 (4)	O1—Si2—O2—Si3	-142.8 (3)
Cu1—O1M	1.978 (4)	Si4—O4	1.627 (4)	O3M—Si3—O2—Si2	20.0 (4)
Cu1—O1S	2.208 (4)	Si4—O3	1.630 (4)	O3—Si3—O2—Si2	140.8 (3)
Cu2—O6M ⁱ	1.947 (4)	Si4—C41	1.856 (6)	O4M—Si4—O3—Si3	-18.2 (4)
Cu2—O2M	1.951 (4)	Si5—O5M	1.618 (4)	O4—Si4—O3—Si3	104.5 (3)
Cu2—O5M ⁱ	1.964 (4)	Si5—O5	1.627 (4)	O3M—Si3—O3—Si4	17.9 (4)
Cu2—O3M	1.967 (4)	Si5—O4	1.641 (4)	O2—Si3—O3—Si4	-103.4 (3)
Cu2—O2S	2.211 (4)	Si5—C51	1.864 (6)	O4M—Si4—O4—Si5	1.9 (4)
Cu3—O1M ⁱ	1.965 (4)	Si6—O6M	1.610 (4)	O3—Si4—O4—Si5	-120.9 (3)
Cu3—O4M	1.967 (4)	Si6—O6	1.628 (4)	O5M—Si5—O4—Si4	1.1 (4)
Cu3—O6M ⁱ	1.972 (3)	Si6—O5	1.639 (4)	O5—Si5—O4—Si4	121.5 (3)
Cu3—O3M	1.975 (4)	Si6—C61	1.866 (6)	O5M—Si5—O5—Si6	-13.5 (4)
Cu3—O3S	2.226 (4)	O1S—C1S	1.226 (7)	O4—Si5—O5—Si6	-134.3 (3)
Si1—O1M	1.612 (4)	N1S—C1S	1.313 (8)	O6M—Si6—O5—Si5	11.5 (4)
Si1—O1	1.631 (4)	O2S—C4S	1.227 (7)	O6—Si6—O5—Si5	133.3 (3)
Si1—O6	1.631 (4)	N2S—C4S	1.322 (7)	O6M—Si6—O6—Si1	11.4 (4)
Si1—C11	1.850 (6)	O3S—C7S	1.214 (7)	O5—Si6—O6—Si1	-109.7 (3)
Si2—O2M	1.605 (4)	N3S—C7S	1.325 (7)	O1M—Si1—O6—Si6	-12.9 (4)
Si2—O1	1.624 (4)	O1SS—C1SS	1.255 (9)	O1—Si1—O6—Si6	108.6 (4)
Si2—O2	1.632 (4)	N1SS—C1SS	1.324 (10)	O6—Si1—O1M—Cu3 ⁱ	-9.0 (4)
Si2—C21	1.856 (6)	O2SS—C4SS	1.248 (10)	O1—Si1—O1M—Cu1	10.9 (3)
Si3—O3M	1.609 (4)	N2SS—C4SS	1.326 (10)	O2M—Cu1—O1M—Si1	-23.0 (3)
Si3—O2	1.634 (4)			O4M ⁱ —Cu1—O1M—Cu3 ⁱ	-30.43 (14)
O2M—Cu1—O5M ⁱ	80.31 (15)	O3—Si3—C31	109.2 (2)	O1—Si2—O2M—Cu1	-19.1 (4)
O2M—Cu1—O4M ⁱ	159.2 (2)	O4M—Si4—O4	111.0 (2)	O2—Si2—O2M—Cu2	26.8 (4)
O5M ⁱ —Cu1—O4M ⁱ	95.55 (15)	O4M—Si4—O3	111.3 (2)	O1M—Cu1—O2M—Si2	28.1 (3)
O2M—Cu1—O1M	95.93 (15)	O4—Si4—O3	108.8 (2)	O5M ⁱ —Cu1—O2M—Cu2	19.8 (2)
O5M ⁱ —Cu1—O1M	160.4 (2)	O4M—Si4—C41	110.0 (2)	O3M—Cu2—O2M—Si2	-25.2 (3)
O4M ⁱ —Cu1—O1M	81.10 (15)	O4—Si4—C41	107.4 (2)	O5M ⁱ —Cu2—O2M—Cu1	-19.85 (15)
O2M—Cu1—C1S	97.8 (2)	O3—Si4—C41	108.1 (2)	O2—Si3—O3M—Cu2	-20.1 (3)
O5M ⁱ —Cu1—O1S	97.8 (2)	O5M—Si5—O5	109.2 (2)	O3—Si3—O3M—Cu3	8.6 (3)
O4M ⁱ —Cu1—O1S	103.0 (2)	O5M—Si5—O4	110.0 (2)	O2M—Cu2—O3M—Si3	21.2 (3)
O1M—Cu1—O1S	101.8 (2)	O5—Si5—O4	110.1 (2)	O6M ⁱ —Cu2—O3M—Cu3	26.92 (14)
O6M ⁱ —Cu2—O2M	162.6 (2)	O5M—Si5—C51	111.7 (2)	O4M—Cu3—O3M—Si3	-23.3 (3)
O6M ⁱ —Cu2—O5M ⁱ	97.1 (2)	O5—Si5—C51	108.4 (2)	O6M ⁱ —Cu3—O3M—Cu2	-26.62 (14)
O2M—Cu2—O5M ⁱ	80.2 (2)	O4—Si5—C51	107.4 (2)	O3—Si4—O4M—Cu3	-8.0 (3)
O6M ⁱ —Cu2—O3M	80.84 (15)	O6M—Si6—O6	111.2 (2)	O4—Si4—O4M—Cu1 ⁱ	12.2 (4)
O2M—Cu2—O3M	96.8 (2)	O6M—Si6—O5	110.0 (2)	O3M—Cu3—O4M—Si4	22.9 (3)
O5M ⁱ —Cu2—O3M	163.57 (15)	O6—Si6—O5	108.5 (2)	O1M ⁱ —Cu3—O4M—Cu1 ⁱ	30.57 (14)
O6M ⁱ —Cu2—O2S	101.0 (2)	O6M—Si6—C61	111.1 (2)	O5—Si5—O5M—Cu2 ⁱ	21.0 (3)
O2M—Cu2—O2S	96.4 (2)	O6—Si6—C61	108.2 (2)	O4—Si5—O5M—Cu1 ⁱ	-19.3 (4)
O5M ⁱ —Cu2—O2S	99.28 (15)	O5—Si6—C61	107.8 (2)	O5—Si6—O6M—Cu2 ⁱ	-16.5 (3)
O3M—Cu2—O2S	97.11 (15)	Si2—O1—Si1	136.0 (2)	O6—Si6—O6M—Cu3 ⁱ	12.2 (3)
O1M ⁱ —Cu3—O4M	81.6 (2)	Si2—O2—Si3	133.6 (2)	Cu1—O1S—C1S—N1S	171.1 (5)
O1M ⁱ —Cu3—O6M ⁱ	95.87 (15)	Si4—O3—Si3	133.3 (2)	C3S—N1S—C1S—O1S	-0.3 (12)
O4M—Cu3—O6M ⁱ	159.21 (15)	Si4—O4—Si5	135.2 (2)	Cu2—O2S—C4S—N2S	-165.7 (5)
O1M ⁱ —Cu3—O3M	159.96 (15)	Si5—O5—Si6	136.3 (2)	C5S—N2S—C4S—O2S	7.6 (10)
O4M—Cu3—O3M	95.2 (2)	Si6—O6—Si1	134.8 (2)	Cu3—O3S—C7S—N3S	179.7 (5)
O6M ⁱ —Cu3—O3M	80.01 (15)	Si1—O1M—Cu3 ⁱ	132.0 (2)	C9S—N3S—C7S—O3S	2.0 (11)
O1M ⁱ —Cu3—O3S	103.2 (2)	Si1—O1M—Cu1	130.4 (2)	C2SS—N1SS—C1SS—O1SS	-2.8 (12)
O4M—Cu3—O3S	102.4 (2)	Cu3 ⁱ —O1M—Cu1	90.14 (15)	C6SS—N2SS—C4SS—O2SS	-2.8 (14)
O6M ⁱ —Cu3—O3S	98.3 (2)	Si2—O2M—Cu1	131.6 (2)		
O3M—Cu3—O3S	96.8 (2)	Si2—O2M—Cu2	130.6 (2)		
O1M—Si1—O1	110.6 (2)	Cu1—O2M—Cu2	96.8 (2)		
O1M—Si1—O6	110.0 (2)	Si3—O3M—Cu2	130.4 (2)		
O1—Si1—O6	109.1 (2)	Si3—O3M—Cu3	132.0 (2)		
O1M—Si1—C11	113.3 (2)	Cu2—O3M—Cu3	92.73 (15)		
O1—Si1—C11	106.6 (2)	Si4—O4M—Cu3	131.3 (2)		
O6—Si1—C11	107.1 (2)	Si4—O4M—Cu1 ⁱ	131.6 (2)		
O2M—Si2—O1	109.6 (2)	Cu3—O4M—Cu1 ⁱ	90.15 (15)		
O2M—Si2—O2	110.1 (2)	Si5—O5M—Cu2 ⁱ	131.0 (2)		
O1—Si2—O2	108.6 (2)	Si5—O5M—Cu1 ⁱ	131.5 (2)		
O2M—Si2—C21	111.3 (2)	Cu2 ⁱ —O5M—Cu1 ⁱ	95.82 (15)		
O1—Si2—C21	107.9 (2)	Si6—O6M—Cu2 ⁱ	131.4 (2)		
O2—Si2—C21	109.3 (2)	Si6—O6M—Cu3 ⁱ	130.5 (2)		
O3M—Si3—O2	110.9 (2)	Cu2 ⁱ —O6M—Cu3 ⁱ	93.42 (15)		
O3M—Si3—O3	110.2 (2)	C1S—O1S—Cu1	123.9 (4)		
O2—Si3—O3	108.0 (2)	C4S—O2S—Cu2	115.7 (4)		
O3M—Si3—C31	112.2 (2)	C7S—O3S—Cu3	114.9 (4)		
O2—Si3—C31	106.2 (2)				
O2M—Si2—O1—Si1	-3.2 (4)				
O2—Si2—O1—Si1	117.1 (3)				
O1M—Si1—O1—Si2	6.6 (4)				

Symmetry code: (i) $-x, 2-y, 1-z$.Refinement was on F^2 for all reflections except for 10 flagged by us for potential systematic errors.Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1396). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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