

motion of these alkyl groups. It should be clear, however, that a unique conformational model involving a statistical average of rotamers cannot be specified from only four NMR observables. Instead there are many closely related rotational models that appear reasonable, but all must have the β -CH₃ groups spending a great majority of the time above the outer OEP ring. One plausible model has the eight β -CH₃ groups centered above the outer OEP ring with $\phi = 0^\circ$. The average geometric factors for an equally populated set of rotamers, $\phi = 0 \pm 60^\circ$, are listed in Table II, and there is good agreement (within 10%) with the experimental dipolar shift ratios.¹⁷ A better fit could, perhaps, be obtained by making minor adjustments in bond lengths and angles; however, such "fine tuning" is not warranted, considering the above limitations. The aforementioned model for reasons of simplicity has the eight β -CH₃ groups above the outer OEP ring at all times. It is also possible to include small excursions of β -CH₃ into the region near the inner OEP ring as long as the mathematical averaging over all rotamer contributions yields the proper geometric factor ratios.

Inner OEP Ring. Three resonances are observed for the meso, α -CH₂, and β -CH₃ protons at -8.12, -5.33, and -5.00 ppm, respectively. With the use of the solid-state geometry as an initial model (vide supra), the respective geometric factors were calculated by assuming equal interaction with both cerium ions. There are three rotational models that preserve the plane of symmetry of the inner OEP: (1) complete and free rotation; (2) restricted rotation centered about $\phi = 270^\circ$ for β -CH₃ (see rotamer A); (3) restricted rotation centered about 90° for β -CH₃. The last model has poor agreement of geometric factors and isotropic shifts and can be discarded. At $\phi = 90^\circ$, adjacent β -CH₃ carbon atoms approach most closely, 1.48 Å, and it seems unlikely that any model of restricted rotation would feature this as its central rotamer.¹⁸ While free rotation of alkyl groups, model 1, offers acceptable mathematical agreement,¹⁹ model 2 is preferable with adjacent β -CH₃ groups being most distant at $\phi = 270^\circ$ and rotating about this position. The best fit is obtained for $\phi = 270 \pm 130^\circ$ as listed in Table II, and this specifically excludes that region of space where the β -CH₃ groups would be in closest proximity.

We have prepared other members of the Ln₂(OEP)₃ series⁵ by the synthetic procedure used for Ce₂(OEP)₃.³ The compounds and their isotropic shifts are listed in Table I. The shifts for Ln = Pr, Nd, and Sm are qualitatively similar—positive β -CH₃ shift, for example—but are too small in magnitude for computer modeling of the geometry. The binuclear Eu₂(OEP)₃ complex also has relatively small isotropic shifts which are opposite in sign to that of Ce₂(OEP)₃ because of a change in sign of $\chi_{\parallel} - \chi_{\perp}$, a change that is anticipated theoretically²⁰ and is consistent with other experimental studies.^{21,22}

In summary, it is apparent that the ¹H dipolar shifts provide compelling evidence for inter-ring steric crowding and subsequent limited rotation of the outer OEP alkyl groups such that the outer β -CH₃ groups stay far away from the inner OEP ring. It also appears likely that there is limited rotation of the inner OEP alkyl groups in order to minimize intra-ring steric crowding.

Experimental Section

All lanthanide(III) tris(octaethylporphyrinates) were prepared by the reaction of octaethylporphyrin and the respective lanthanide(III) tris(acetylacetonate) in refluxing trichlorobenzene under a nitrogen atmosphere as described in detail elsewhere for Ce₂(OEP)₃³ and Eu₂(OEP)₃.⁶ Except for Eu₂(OEP)₃, the percent yield decreased with each successive lanthanide, and no product could be isolated for Ln = Gd-Lu.

The ¹H NMR spectra were obtained on a Bruker WM 300-MHz spectrometer as previously described.³

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Contribution from the Chemistry Department, D-006, University of California at San Diego, La Jolla, California 92093, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Preparation and Characterization of the Monomeric Copper(II) Siloxide Complex Cu[OSi(OCMe₃)₃]₂(py)₂

Anne K. McMullen,[†] T. Don Tilley,^{*†} Arnold L. Rheingold,^{*‡} and Steven J. Geib[‡]

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Trialkoxysiloxy ligands, -OSi(OR)₃, have not been extensively employed in transition-metal chemistry. Our interest in these ligands stems from their potential to form new types of siloxy complexes with interesting chemical properties. For example, M-OSi(OR)₃ complexes may exhibit properties that resemble catalytic metal species supported on a silica surface.¹ Also, such compounds may serve as convenient molecular precursors to oxide and silicate materials via hydrolysis or thermolysis.^{2,3} To our knowledge, the only transition-metal trialkoxysiloxy complexes that have been reported are the titanium derivatives (RO)₃TiOSi(OR)₃ (R = ⁿPr,⁴ ^tBu⁵), [(^tBuO)₃SiO]₂Ti(OⁱPr),³ and [(^tBuO)₃SiO]₂TiX₂ (X = OⁱPr, acac)³ and the zirconium complexes Zr[OSi(OⁱBu)]₃⁶ and [(^tBuO)₃SiO]₂ZrX₂ (X = OⁱPr, acac).⁶

Here we report the synthesis, characterization, and molecular structure of the copper(II) siloxide complex Cu[OSi(OⁱBu)]₃₂(py)₂. This compound is unusual, since copper(II) alkoxides are generally highly associated and insoluble.⁷ In addition, siloxy derivatives of copper are quite rare, and no well-characterized examples appear to have been reported for copper(II). An ill-defined siloxy complex, (Ph₂SiO)_x(CuO)_y, formed by addition of Ph₂(ONa)-SiOSi(ONa)Ph₂ to CuCl₂, was reported to rapidly decompose to CuO and *c*-Ph₈Si₄O₄,⁸ although Cu[OSi(OH)₂Ph]₂ and related polymeric derivatives have been claimed.⁹ Schmidbauer has reported a series of copper(I) compounds, [CuOSiMe₃]₄ and (Me₃P)_xCuOSiMe₃ (x = 1-3), that are polymeric with bridging siloxide ligands.¹⁰

Results and Discussion

Addition of 2 equiv of NaOSi(OⁱBu)₃ to CuBr₂ in tetrahydrofuran results in a yellow solution from which a mixture of green and yellow crystals can be isolated. Numerous attempts failed to separate these products by fractional crystallization or to drive the reaction to a single product by changing reaction conditions. These products have therefore not been characterized, but we know that neither contains solvent or bromide. This mixture therefore probably contains {CuOSi(OⁱBu)₃}_n and/or {Cu[OSi(OⁱBu)₃]₂}_n species.

A single copper(II) siloxide complex, Cu[OSi(OⁱBu)]₃₂(py)₂, was isolated by addition of pyridine to the above reaction mixture. This paramagnetic ($\mu_{\text{eff}} = 1.16 \mu_{\text{B}}$ at 34 °C in benzene solution; Evans method¹¹) complex is pale green and soluble in saturated hydrocarbons. Because there is a great lack of structural data

(17) If rotation becomes more extensive, however, the agreement between relative values of *G* and $\Delta H/H$ progressively worsens.

(18) The adjacent β -CH₃ group in the symmetry-equivalent conformation has $\phi = 270^\circ$.

(19) The geometric factors for free rotation are as follows: meso, -0.004 84 Å⁻³; α -CH₂, -0.002 83 Å⁻³; β -CH₃, -0.002 46 Å⁻³.

(20) Golding, R. M.; Pyykkö, P. *Mol. Phys.* **1973**, *26*, 1389.

(21) Horrocks, W. D., Jr.; Sipe, J. P., III. *Science* **1972**, *177*, 994.

(22) Alsaadi, B. M.; Rossotti, F. J. C.; Williams, R. J. P. *J. Chem. Soc., Dalton Trans.* **1980**, 597.

[†]University of California, San Diego.

[‡]University of Delaware.

Table I. Crystallographic Data for $\text{Cu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{py})_2$

chem formula $\text{C}_{34}\text{H}_{64}\text{CuN}_2\text{O}_8\text{Si}_2$ fw 748.57	space group $P2_1/n$ (No. 14) $T = 22^\circ\text{C}$
$a = 14.146$ (4) Å	$\lambda = 0.71073$ Å (Mo K α)
$b = 17.398$ (5) Å	$\rho_{\text{calc}} = 1.140$ g cm $^{-3}$
$c = 18.566$ (6) Å	$\mu = 5.96$ cm $^{-1}$
$\beta = 107.36$ (3) $^\circ$	transm coeff = 0.72–0.67
$V = 4362$ (2) Å 3	$R(F) = 6.04\%$
$Z = 4$	$R(wF) = 6.13\%$

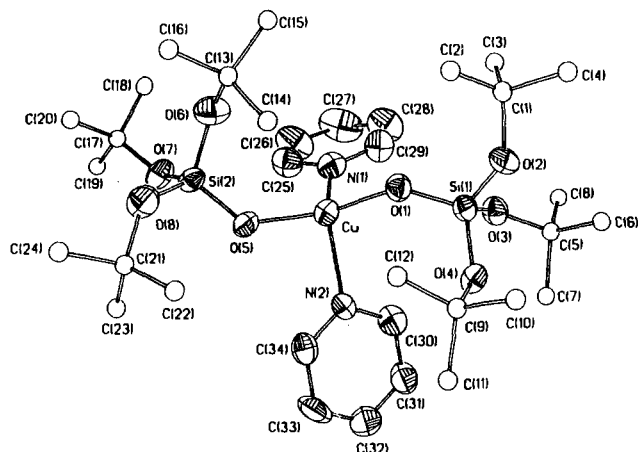
Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for $\text{Cu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{py})_2$

	x	y	z	U^a
Cu	4852.9 (9)	4616.0 (7)	2903.3 (7)	50.2 (5)
Si(1)	3122 (2)	4063 (2)	1409 (2)	45 (1)
Si(2)	6835 (2)	5546 (2)	3554 (2)	49 (1)
O(1)	3889 (4)	4587 (4)	1988 (3)	55 (3)
O(2)	2732 (4)	4422 (4)	561 (3)	57 (3)
O(3)	2207 (4)	3924 (4)	1753 (3)	57 (3)
O(4)	3529 (4)	3212 (3)	1299 (3)	49 (3)
O(5)	6170 (5)	4807 (3)	3436 (4)	58 (3)
O(6)	6319 (5)	6259 (4)	3005 (4)	76 (4)
O(7)	7000 (5)	5841 (4)	4404 (4)	63 (3)
O(8)	7892 (5)	5406 (4)	3393 (4)	74 (3)
C(1)	2520 (9)	5195 (6)	292 (6)	69 (6)
C(2)	3459 (10)	5569 (8)	261 (8)	134 (9)
C(3)	2036 (12)	5632 (7)	751 (8)	153 (10)
C(4)	1841 (12)	5114 (8)	-508 (8)	138 (9)
C(5)	1320 (8)	3442 (8)	1549 (7)	70 (6)
C(6)	946 (9)	3343 (9)	706 (7)	125 (8)
C(7)	1564 (8)	2668 (7)	1928 (7)	91 (6)
C(8)	568 (8)	3846 (7)	1849 (8)	120 (8)
C(9)	4293 (7)	2964 (6)	988 (6)	57 (5)
C(10)	3811 (9)	2847 (7)	146 (7)	102 (7)
C(11)	4660 (9)	2205 (7)	1355 (7)	99 (7)
C(12)	5122 (8)	3534 (7)	1117 (8)	106 (7)
C(13)	6227 (8)	6464 (6)	2245 (6)	75 (5)
C(14)	6084 (9)	5751 (7)	1755 (6)	93 (6)
C(15)	5308 (10)	6972 (8)	2003 (8)	129 (8)
C(16)	7126 (9)	6898 (8)	2209 (7)	120 (8)
C(17)	7402 (8)	6520 (6)	4804 (6)	74 (6)
C(18)	6605 (11)	7098 (8)	4669 (11)	200 (12)
C(19)	7648 (14)	6344 (9)	5612 (9)	209 (14)
C(20)	8214 (13)	6851 (11)	4597 (11)	244 (15)
C(21)	8524 (7)	4746 (6)	3466 (7)	75 (5)
C(22)	8115 (10)	4232 (7)	2768 (7)	125 (8)
C(23)	8633 (10)	4331 (7)	4189 (7)	122 (8)
C(24)	9522 (8)	5097 (7)	3461 (8)	117 (8)
N(1)	4075 (8)	5264 (5)	3454 (5)	62 (4)
C(25)	4528 (9)	5551 (6)	4165 (7)	79 (6)
C(26)	3974 (9)	5861 (8)	4585 (7)	103 (7)
C(27)	2995 (11)	5913 (9)	4307 (9)	117 (9)
C(28)	2516 (11)	5644 (8)	3589 (8)	105 (8)
C(29)	3105 (10)	5324 (7)	3186 (7)	72 (6)
N(2)	4934 (6)	3431 (4)	3216 (4)	51 (4)
C(30)	4111 (8)	3039 (7)	3126 (6)	63 (5)
C(31)	4133 (9)	2278 (7)	3352 (6)	76 (6)
C(32)	5006 (9)	1917 (7)	3658 (7)	85 (6)
C(33)	5859 (8)	2306 (6)	3756 (6)	86 (6)
C(34)	5794 (8)	3084 (6)	3531 (6)	62 (5)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

for copper(II) alkoxide complexes with monodentate alkoxy ligands and since no copper(II) siloxide complex has been structurally

- (1) (a) Hartley, F. R. *Supported Metal Complexes*; Reidel: Boston, MA, 1985. (b) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: New York, 1981. (c) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741. (d) Rodriguez, E.; Leconte, M.; Basset, J. M.; Tanaka, K.; Tanaka, K.-I. *J. Am. Chem. Soc.* **1988**, *110*, 275. (e) Gates, B. C. In *Metal Clusters*; Moskovits, M., Ed.; Wiley: New York, 1986; p 283. (f) Walter, T. H.; Frauenhoff, G. R.; Shapley, J. R.; Oldfield, E. *Inorg. Chem.* **1988**, *27*, 2561. (g) Vizi-Orosz, A.; Marko, L. *Transition Met. Chem. (Weinheim, Ger.)* **1982**, *7*, 216. (h) Bruce, G. C.; Stobart, S. R. *Inorg. Chem.* **1988**, *27*, 3879 and references in the above.

**Figure 1.** ORTEP view of $\text{Cu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{py})_2$ with atom-labeling scheme.**Table III.** Selected Bond Distances and Angles

(a) Bond Distances (Å)			
Cu–O(1)	1.835 (5)	Si(2)–O(6)	1.633 (7)
Cu–O(5)	1.861 (6)	Si(2)–O(7)	1.610 (7)
Cu–N(1)	2.049 (11)	Si(2)–O(8)	1.628 (8)
Cu–N(2)	2.136 (8)	Si(1)–O(1)	1.571 (6)
Si(1)–O(2)	1.630 (6)	Si(1)–O(3)	1.623 (8)
Si(1)–O(4)	1.622 (7)	Si(2)–O(5)	1.570 (7)
(b) Bond Angles (deg)			
O(1)–Cu–O(5)	147.9 (3)	O(1)–Cu–N(1)	96.7 (3)
O(5)–Cu–N(1)	103.8 (3)	O(1)–Cu–N(2)	100.9 (3)
O(5)–Cu–N(2)	93.7 (3)	N(1)–Cu–N(2)	112.9 (4)
O(1)–Si(1)–O(2)	113.8 (4)	O(1)–Si(1)–O(3)	106.6 (4)
O(2)–Si(1)–O(3)	111.0 (3)	O(1)–Si(1)–O(4)	114.6 (3)
O(2)–Si(1)–O(4)	105.0 (3)	O(3)–Si(1)–O(4)	105.5 (4)
O(5)–Si(2)–O(6)	113.4 (3)	O(5)–Si(2)–O(7)	107.6 (4)
O(6)–Si(2)–O(7)	106.1 (4)	O(5)–Si(2)–O(8)	113.3 (4)
O(6)–Si(2)–O(8)	105.3 (4)	O(7)–Si(2)–O(8)	110.9 (4)
Cu–O(1)–Si(1)	145.1 (4)	Si(1)–O(2)–C(1)	132.2 (6)
Si(1)–O(3)–C(5)	135.0 (7)	Si(1)–O(4)–C(9)	131.4 (6)
Cu–O(5)–Si(2)	133.1 (4)	Si(2)–O(6)–C(13)	134.5 (7)
Si(2)–O(7)–C(17)	134.1 (7)	Si(2)–O(8)–C(21)	133.0 (7)

characterized, an X-ray crystal structure determination was undertaken.

The structure of $\text{Cu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{py})_2$ consists of well-separated monomeric units. For comparison, no monomeric copper complexes with monodentate alkoxy or aryloxy ligands have been structurally characterized, but a related compound having two aryloxy ligands and two nitrogen donors per copper atom, $[\text{Cu}(\text{OPh})_2(\text{en})]_2 \cdot 2\text{PhOH}$, is dimeric with bridging phenoxy groups.¹² An ORTEP view of $\text{Cu}[\text{OSi}(\text{O}^t\text{Bu})_3]_2(\text{py})_2$ is shown in Figure 1. Crystal and data collection parameters are summarized in Table

- (2) (a) Hardy, A. B.; Gowda, G.; McMahon, T. J.; Riman, R. E.; Rhine, W. E.; Bowen, H. K. In *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; p 407. (b) Chaput, F.; Lecomte, A.; Dauger, A.; Boilot, J. P. *Chem. Mater.* **1989**, *1*, 199.
- (3) Abe, Y.; Kijima, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 466.
- (4) Varma, I. D.; Mehrotra, R. C. *J. Prakt. Chem.* **1959**, *8*, 235.
- (5) Nesmeyanov, A. N.; Nogina, O. V. *Dok. Akad. Nauk SSSR* **1957**, *117*, 249.
- (6) Abe, Y.; Hayama, K.; Kijima, I. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1258.
- (7) (a) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269. (b) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.
- (8) Hornbaker, E. D.; Conrad, F. J. *Org. Chem.* **1959**, *24*, 1858.
- (9) Zhdanov, A. A.; Andrianov, K. A.; Levitskii, M. M. *Vysokomol. Soyedin.* **1976**, *A18*, 2264 (translated in *Polym. Sci. USSR (Engl. Transl.)* **1976**, *18*, 2590).
- (10) Schmidbauer, H.; Adlkofer, J.; Shiotani, A. *Chem. Ber.* **1972**, *105*, 3389.
- (11) Evans, D. F.; James, T. A. *J. Chem. Soc., Dalton Trans.* **1979**, 723.
- (12) Calderazzo, F.; Marchetti, F.; Dell'Amico, G.; Pelizzi, G.; Colligiani, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1419.

I, and relevant geometrical parameters are given in Tables II and III.

The coordination geometry can be described as a severely distorted tetrahedron, with angles at the copper atom ranging from 93.7 (3) to 147.9 (3)°. These angles may to some degree reflect different steric requirements of the ligands and a high degree of steric crowding. Consistent with the description of the structure as a distorted tetrahedron, the angle between the CuO₂ and CuN₂ planes is 85.6°.

The Cu–N(py) bond distances in the molecule, 2.049 (11) and 2.136 (8) Å, are very similar to corresponding distances in related structures of the type Cu(η^2 -OAr)₂(py)₂, in which the aryl group has a donor atom in the ortho position.¹³ However, the Cu–O(siloxide) distances, 1.861 (6) and 1.835 (5) Å, are considerably shorter than analogous distances in the latter compounds (these values range from 1.89 to 1.97 Å).¹³ Given its smaller coordination number, Cu[OSi(O^tBu)₃]₂(py)₂ might be expected to have shorter Cu–L distances than the Cu(η^2 -OAr)₂(py)₂ complexes. The Cu–O–Si angles (133.1 (4) and 145.1 (4)°) and the Si–O bond distances (average 1.61 Å) are within the ranges expected for silicate-type structures.¹⁴ However, the Cu–O–Si angles are somewhat smaller than other M–O–Si angles that have been observed in transition-metal siloxide complexes.¹⁵

Initial attempts to convert Cu[OSi(O^tBu)₃]₂(py)₂ to a solid-state material via hydrolysis were undertaken. Hydrolysis with excess water in benzene solution gave a dark brown precipitate, presumably CuO, and a quantitative yield of the silanol (^tBuO)₃SiOH (by ¹H NMR spectroscopy). Future reports will describe thermalyses of Cu[OSi(O^tBu)₃]₂(py)₂ and related complexes.

Experimental Section

Manipulations were conducted under an atmosphere of nitrogen or argon by using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Mikroanalytisches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 instrument. ¹H NMR spectra were recorded at 300 MHz with a GE QE-300 instrument

or at 90 MHz with a Varian EM-390 instrument. The magnetic moment was determined by the Evans method¹¹ in benzene solution at 90 MHz. The silanol (^tBuO)₃SiOH was prepared from (^tBuO)₃SiCl by the literature procedure.¹⁶

NaOSi(O^tBu)₃. A solution of (^tBuO)₃SiOH (30.0 g, 0.113 mol) in pentane (250 mL) was added dropwise to a cooled (0 °C) suspension of Na (3.00 g, 0.130 mol) in pentane (100 mL). After being stirred at 0 °C for 4 h, the reaction mixture was warmed to room temperature and filtered. Concentration and cooling (–78 °C) of the resulting solution yielded NaOSi(O^tBu)₃ in 99% yield (32.2 g). Anal. Calcd for C₁₂H₂₇NaO₄Si: C, 50.3; H, 9.50. Found: C, 50.9; H, 9.58. IR (Nujol, CsI; cm⁻¹): 1360 s, 1240 s, br, 1215 m sh, 1195 vs, br, 1070 vs, br, 1038 vs, br, 1020 vs, br, 1000 vs, br, 910 w, 820 s, 700 s, br, 690 s sh, 515 m, 490 m, 475 w sh, 420 w, 388 vw, 345 vw, 305 w, br. ¹H NMR (benzene-*d*₆, 300 MHz, 22 °C): δ 1.48 (s).

Cu[OSi(O^tBu)₃]₂(py)₂. CuBr₂ (0.50 g, 2.24 mmol) and NaOSi(O^tBu)₃ (1.28 g, 4.47 mmol) were stirred together in tetrahydrofuran (50 mL) for 14 h, resulting in a dark yellow solution. Volatiles were removed in vacuo to afford a pale green solid, to which pentane (50 mL) was added. Pyridine (1.8 mL, ca. 10 equiv) was added to the dark green pentane solution, and the mixture was stirred for 5 min and filtered. The dark green filtrate was evacuated to dryness, and the resulting residue was recrystallized from pentane to afford pale green crystals. Yield: 0.24 g (14.0%). Anal. Calcd for C₃₄H₆₄CuNO₈Si₂: C, 54.6; H, 8.62; N, 3.74. Found: C, 54.2; H, 8.70; N, 3.68. IR (Nujol, CsI; cm⁻¹): 1605 m, 1450 m, 1360 s, 1240 m, br, 1210 m, 1195 s, 1055 s, br, 1044 s, br, 1024 s, br, 1005 s, br, 822 m, 754 w, 695 s, 645 vw, br, 515 vw, br, 480 vw, br, 425 vw, br, 280 vw, br.

X-ray Structure Determination. A summary of crystallographic data is provided in Table I. Crystals were mounted in glass capillary tubes in an inert-atmosphere glovebox and then flame-sealed. All crystals that were examined diffracted very weakly. Data were collected to the limits of availability ($2\theta = 43^\circ$) on a Nicolet R3m diffractometer at room temperature using a pale green specimen (0.25 × 0.31 × 0.36 mm). Of 5418 data empirically corrected for absorption, 5012 were independent, and 2264 with $F_o \geq 3\sigma(F_o)$ were retained as observed. The Cu and Si atoms were located by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI).

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Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

- (13) (a) Bullock, J. I.; Hobson, R. J.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1974**, 2037. (b) Ladd, M. F. C.; Perrins, D. H. G. *Acta Crystallogr.* **1980**, *B36*, 2260. (c) Wong, R. Y.; Palmer, K. J.; Tomimatsu, Y. *Acta Crystallogr.* **1976**, *B32*, 567. (d) Greenhough, T. J.; Ladd, M. F. C. *Acta Crystallogr.* **1978**, *B34*, 2619. (e) Greenhough, T. J.; Ladd, M. F. C. *Acta Crystallogr.* **1978**, *B34*, 2744.
- (14) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: New York, 1985.
- (15) (a) Babaian, E. A.; Hrcncir, D. C.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 4818. (b) Klemperer, W. G.; Mainz, V. V.; Wang, R.-C.; Shum, W. *Inorg. Chem.* **1985**, *24*, 1970. (c) Young, K. D.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1831. (d) Sigel, G. A.; Bartlett, R. A.; Decker, D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 1773.

- (16) Abe, Y.; Kijima, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1118.