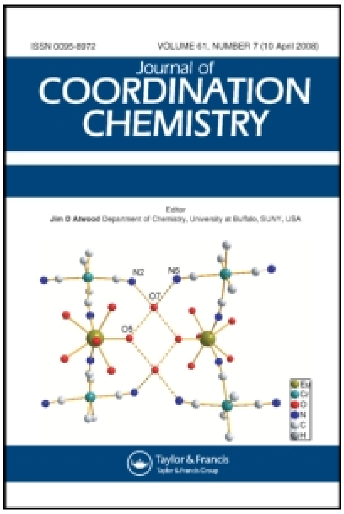

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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE DILITHIUM COPPER SILOXIDE $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2\ [Li(THF)_2]_2$

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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE DILITHIUM COPPER SILOXIDE $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$*

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$CuCl_2$ reacts with four equivalents of $Ph_2SiO_2Li_2$ in THF to form $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$ in 80% yield by formal elimination of Li_2O and LiCl. $CuBr_2$ reacts analogously. The product of these reactions has a spirocyclic metallasiloxane structure containing two CuOSiOSiO and two CuOLiO rings.

Keywords: Siloxide; spirocyclic metallasiloxane; heterometallic; copper

INTRODUCTION

The synthesis of heterometallic complexes with a variety of metallic components in specific stoichiometries is necessary to use molecular chemistry to make homogeneous precursors to materials containing mixed metallic compositions.[1–3] The bimetallic nature of the dilithiosiloxide complex $Ph_2Si(OLi)_2$, **1** ($Ph = C_6H_5$), suggested that the $[Ph_2SiO_2]^{2-}$ unit could be a useful dianionic ligand with which to connect two metal centers. We have investigated the reaction of **1** with copper salts to see if the lithium atoms could be replaced by copper such that the ligand could be used to bridge copper to other metals.[4–7] We report here a novel result in which a

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heterometallic spirocyclic metallasiloxane containing copper and two lithium ions is isolated.[8-12]

EXPERIMENTAL

The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line and glove box techniques. $Ph_2Si(OLi)_2$ was prepared from $Ph_2Si(OH)_2$ (Huls) and *n*-butyl lithium (Aldrich) and was heated at 50°C under vacuum (10^{-5} torr) for 24 h before use. No change in the infrared spectrum was noted due to this heating. Anhydrous $CuCl_2$ and $CuBr_2$ (Aldrich) were degassed before use. The solvents were dried and degassed as previously described.[13] NMR spectra were recorded on a Bruker 250 MHz spectrometer or DRX 400 MHz spectrometer. Infrared spectra were obtained on a Perkin Elmer 1600 FTIR spectrometer. Elemental analyses were done by Analytische Laboratorien, D-51779 Lindlar, Germany.

$Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, 2

Colorless $Ph_2Si(OLi)_2$ (338 mg, 1.48 mmol) was added to a mixture of dark yellow $CuCl_2$ (50 mg, 0.37 mmol) in THF (15 ml) producing a blue solution within 2 min. After stirring for 2 days, a pale blue precipitate was separated from the deep blue solution by centrifugation. The solvent was removed from the blue solution by rotary evaporation and the blue product was extracted with toluene and separated from the insoluble material by centrifugation. The toluene was removed from the blue solution and the solid was recrystallized from a mixture of THF/toluene yielding blue $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, **2** (370 mg, 80%). Anal: Calcd. for $C_{64}H_{72}CuLi_2O_{10}Si_4$: C, 64.54; H, 6.09; Cu, 5.34; Li, 1.17; Si, 9.43. Found: C, 64.38; H, 6.03; Cu, 5.14; Li, 1.09; Si, 9.30. ^1H NMR (THF-d_8): δ 8.5 (br s), 7.7 (br s), 3.6 (v br). 1.4 (br). IR (KBr): 3557 br m, 3044 m, 2966 m, 2872 m, 1957 w, 1890 w, 1825 w, 1588 m, 1484 w, 1426 s, 1296 w, 1261 m, 1185 w, 1114 s, 1044 s, 967 s, 914 s, 798 w, 741 m, 702 s cm^{-1}. Similarly, **2** can be prepared using $CuBr_2$ with yields exceeding 80%.

X-ray Data Collection, Structure Determination, and Refinement for $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, 2

A pale blue crystal of approximate dimensions 0.33 × 0.43 × 0.43 mm was immersed in Paratone-N oil under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Siemens P3

TABLE I Experimental data for the X-ray diffraction studies of $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, **2**

Formula	$C_{64}H_{72}Li_2O_{10}Si_4Cu \cdot C_7H_8$
FW	1283.1
Temp. (K)	173
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	14.045(2)
b(Å)	13.814(2)
c(Å)	17.412(3)
β (deg)	94.398(12)
Volume (Å^3)	3368.1(8)
Z	2
$D_{\mathrm{calcd.}}$ (Mg/m^3)	1.27
Diffractometer	Siemens P3 (R3m/V System)
Limiting indices	$0 \leq h \leq 15, 0 \leq K \leq 14, -18 \leq l \leq 18$
Scan width, in ω	1.2° plus Kα separation
Scan speed, in ω (deg min^{-1})	3.0
2θ Range (deg)	4.0–45
Absorption coefficient, μ (mm^{-1})	0.0448
Absorption correction	None
F(000)	1354
Reflections collected	4874
Independent reflections	4135 ($R_{\mathrm{int}} = 1.18\%$)
Observed reflections $[\lvert F_0\rvert > 2\sigma(\lvert F_o\rvert)]$	3871
Refinement method	Full-matrix least-squares
Data/restraints/parameters	1736/0/175
Refinement $[\lvert F_o\rvert > 2\sigma(\lvert F_o\rvert)]$	R_F, 4.8%; R_{wF}, 5.8%
Refinement (all data)	R_F, 5.3%; R_{wF}, 5.8%
Goodness of fit	1.53

Radiation: MoKα ($\lambda = 0.71973$ Å)
Monochromator: highly oriented graphite
$R_F = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$;
$R_{wF} = [\Sigma w(||F_O| - |F_c||)/\Sigma w|F_o|]$

diffractometer which is equipped with a modified LT-2 apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low temperature (173 K) intensity data were carried out using standard techniques similar to those of Churchill *et al.*[14] Experimental details appear in Table I.

All 4874 data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\mathrm{net}) < 0$ was assigned the value $|F_o| = 0$. A careful examination of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a non-standard setting of $P2_1/c[C^5_{2h}$; No.14], is thus uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[15] or the SHELXTL PLUS program set.[16] The analytical scattering factors for

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic* displacement coefficients ($Å^2 \times 10^3$) for $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, **2**

	x	*y*	*z*	*U*(eq)	*S.O.F*
Cu(1)	0	0	0	22.0(.2)	
Si(1)	−1187(1)	1087(1)	−1370(1)	24.5(.3)	
Si(2)	−1544(1)	1696(1)	199(1)	24.5(.3)	
O(1)	−715(2)	140(2)	−977(1)	29(1)	
O(2)	−1656(2)	1794(2)	−743(1)	27(1)	
O(3)	−632(2)	1071(2)	489(1)	29(1)	
C(1)	−2177(2)	745(2)	−2097(2)	25(1)	
C(2)	−1979(3)	318(3)	−2794(2)	36(1)	
C(3)	−2701(3)	11(3)	−3327(2)	44(1)	
C(4)	−3639(3)	141(3)	−3177(2)	44(1)	
C(5)	−3858(3)	558(3)	−2492(2)	43(1)	
C(6)	−3139(3)	856(3)	−1965(2)	36(1)	
C(7)	−273(2)	1809(3)	−1846(2)	28(1)	
C(8)	659(3)	1466(3)	−1877(2)	46(2)	
C(9)	1338(3)	1998(4)	−2229(3)	60(2)	
C(10)	1117(3)	2875(3)	−2556(2)	51(2)	
C(11)	217(3)	3236(3)	−2523(2)	49(2)	
C(12)	−472(3)	2709(3)	−2176(2)	38(1)	
C(13)	−2667(3)	1127(3)	499(2)	30(1)	
C(14)	−3556(3)	1562(3)	314(2)	42(1)	
C(15)	−4396(3)	1121(4)	498(3)	61(2)	
C(16)	−4373(4)	246(5)	869(3)	67(2)	
C(17)	−3522(4)	−192(3)	1053(3)	62(2)	
C(18)	−2677(2)	238(3)	872(2)	47(2)	
C(19)	−1480(2)	2975(3)	566(2)	27(1)	
C(20)	−1216(3)	3726(3)	106(2)	40(1)	
C(21)	−1161(3)	4672(3)	374(2)	46(2)	
C(22)	−1361(3)	4883(3)	1116(3)	46(2)	
C(23)	−1608(3)	4152(3)	1581(3)	58(2)	
C(24)	−1680(3)	−3214(3)	1309(2)	49(2)	
Li(1)	3301(4)	1080(4)	1323(3)	28(2)	
O(4)	1287(2)	2052(2)	1173(7)	48(1)	
C(25)	1319(4)	2535(4)	460(3)	80(2)	
C(26)	2237(5)	2339(7)	177(4)	131(4)	
C(27)	2799(4)	1812(5)	800(4)	98(3)	
C(28)	2244(3)	1934(4)	1481(3)	61(2)	
O(5)	−59(2)	1257(2)	2391(1)	40(1)	
C(29)	447(3)	1920(4)	2911(3)	69(2)	
C(30)	−161(4)	2130(5)	3534(3)	85(2)	
C(31)	1121(3)	1746(4)	3289(3)	68(2)	
C(32)	−938(3)	992(3)	2701(3)	51(2)	
Disordered toluene solvent molecule					
C(33)	5844(4)	5019(7)	−11(5)	83(3)	1.00
C(34)	5945(14)	4292(13)	465(11)	110(7)	0.50
C(35)	5119(9)	3822(6)	820(5)	126(5)	1.00
C(36)	4218(15)	4307(13)	468(9)	96(7)	0.50
C(37)	5052(12)	4546(9)	345(6)	77(6)	0.50

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

neutral atoms were used throughout the analysis;[17a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[17b] were included. The quantity minimized during least-squares analysis was $\Sigma w(|F_o|-|F_c|)^2$ where $w^{-1}=\sigma^2(|F_o|)+0.0007(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The molecule lies on an inversion center with Cu(1) at 0, 0, 0. There is a disordered toluene solvent molecule in the crystal lattice which is also located about an inversion center (1/2, 1/2, 0). Hydrogen atom contributions were included using a riding model with $d(\text{C–H})=0.96\,\text{Å}$ and $U(\text{iso})=0.08\,\text{Å}^2$ (those eight hydrogens of the disordered toluene were not included). Atomic coordinates and equivalent isotropic displacement coefficients appear in Table II. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F=4.8\%$, $R_{wF}=5.8\%$ and GOF $=1.53$ for 413 variables refined against those 3817 data with $|F_o|>2.0\,\sigma(|F_o|)$, ($R_F=3.8\%$; $R_{wF}=5.4\%$ for those 3311 data with $|F_o|>6.0\,\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features, $\rho(\text{max})=0.27\,e\,\text{Å}^{-3}$.

RESULTS AND DISCUSSION

Both $CuCl_2$ and $CuBr_2$ react readily with THF solutions of $Ph_2Si(OLi)_2$, **1**, to form blue/green colored solutions. The ^1H NMR spectra of the solid products isolated were not structurally definitive: only broad phenyl and THF resonances were observed. Crystals were grown from a mixture of toulene/THF by slow evaporation and an X-ray diffraction study revealed the structure shown in Figure 1.

Complex **2** no longer contains the simple $[Ph_2SiO_2]^{2-}$ ligand. Instead, a dianion of the formula $[OPh_2SiOSiPh_2O]^{2-}$ is present. The formation of this ligand can be envisaged as formally involving the elimination of Li_2O as shown in Eq. (1).

$$CuCl_2 + \underset{1}{4Ph_2SiO_2Li_2} + 4THF \xrightarrow{THF} \underset{2}{Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2} + 2LiCl + 2Li_2O \qquad (1)$$

a transformation with analogies in the elimination of H_2O in sol–gel condensations. It is interesting to note that the reaction of $CuCl_2$ with $Ph_2Si(ONa)_2$ is reported to form CuO and $(Ph_2SiO)_4$ *via* a "short-lived colored intermediate."[18] Reactions between $CuCl_2$ and $Ph_2Si(OLi)_2$ run with the proper stoichiometry to give **2**, form this blue complex in 80% yield based on copper.

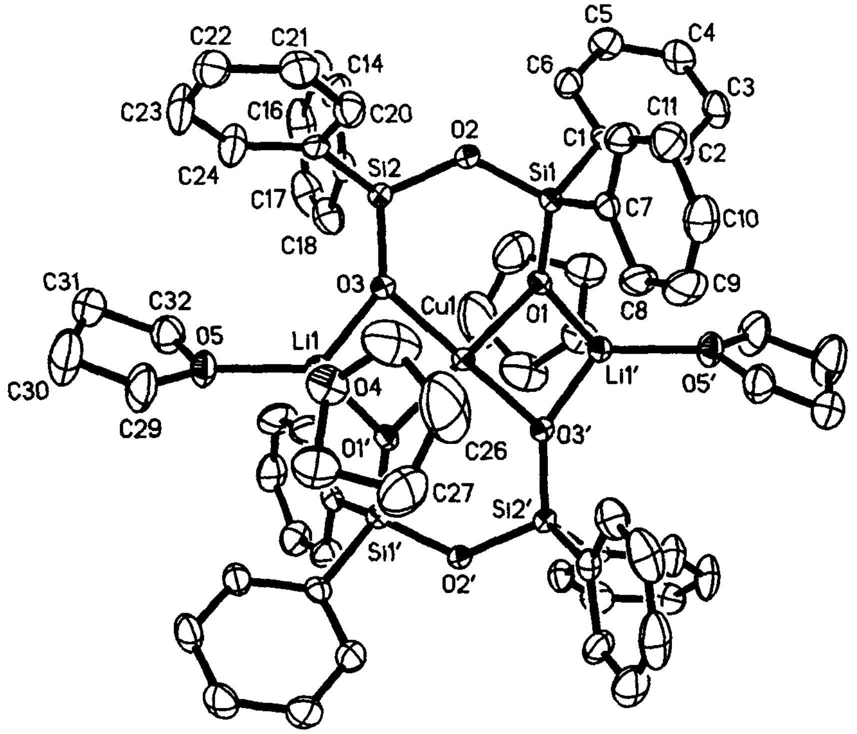

FIGURE 1 Thermal ellipsoid plot of Cu(μ-OSiPh$_2$OSiPh$_2$O)$_2$[Li(THF)$_2$]$_2$, **2**, drawn at the 40% probability level.

Structural data on **2** are presented in Table III. Except for the fact that **2** has an inversion center, the structure is analogous to that of Cu(μ-OSiPh$_2$OSiPh$_2$O)$_2$[Li(pyridine)$_2$]$_2$, **3**, made from CuCl$_2$ and Co(μ-OSiPh$_2$OSiPh$_2$O)$_2$[Li(tmeda)]$_2$,[9] which is made from CoCl$_2$ and Li$_2$[OSi-Ph$_2$OSiPh$_2$O].[10] Complex **2**, like **3**, contains copper in a square-planar environment of Cu—O bonds. However, unlike **3** which has a distorted square-planar geometry, the copper and the four coordinated oxygen atoms of **2** are perfectly planar. The two unique O—Cu—O angles, 94.9(1)° and 85.1(1)°, are similar to the 86.0(4)°–96.7(4)° range of the four O—Cu—O angles in **3**. The 1.918(2) and 1.953(2) Å Cu—O bond distances in **2** are within the error limits of the 1.896(8)–1.944(8)Å analogs in **3**. The lithium atoms in **2** are tetrahedrally coordinated with shorter connections to the siloxide oxygens (1.879(6) and 1.895(6) Å) than to the THF oxygen atoms (1.961(6) and 1.980(6) Å) as expected.

TABLE III Selected bond distances (Å) and angles (°) for $Cu(\mu\text{-}OSiPh_2OSiPh_2O)_2[Li(THF)_2]_2$, **2**

Cu(1)–O(1)	1.918(2)	Cu(1)–O(3)	1.953(2)
Cu(1)...Li(1)	2.749(5)		
Si(1)–O(1)	1.597(2)	Si(1)–O(2)	1.640(2)
Si(2)–O(2)	1.641(2)	Si(2)–O(3)	1.595(2)
Si(1)–C(1)	1.868(3)	Si(1)–C(7)	1.870(4)
Si(2)–C(13)	1.872(4)	Si(2)–C(19)	1.878(4)
Li(1)–O(4)	1.961(6)	Li(1)–O(1′)	1.895(6)
Li(1)–O(3)	1.879(6)	Li(1)–O(5)	1.980(6)
O(1)–Cu(1)–O(3)	94.9(1)	O(3)–Cu(1)–O(1′)	85.1(1)
Cu(1)–O(1)–Si(1)	129.4(1)	Cu(1)–O(3)–Si(2)	130.8(1)
Cu(1)–O(1)–Li(1′)	92.3(2)	Cu(1)–O(2)–Li(1)	91.6(2)
O(1)–Si(1)–O(2)	112.2(1)	O(2)–Si(2)–O(3)	111.9(1)
O(1)–Si(1)–C(1)	110.2(1)	O(2)–Si(1)–C(1)	106.6(1)
O(1)–Si(1)–C(7)	110.5(1)	O(2)–Si(1)–C(7)	107.6(1)
O(2)–Si(2)–C(13)	107.2(1)	O(2)–Si(2)–C(19)	105.1(1)
O(3)–Si(2)–C(13)	111.0(1)	O(3)–Si(2)–C(19)	112.7(1)
C(1)–Si(1)–C(7)	109.5(1)	C(13)–Si(2)–C(19)	108.6(2)
Si(2)–O(3)–Li(1)	137.4(2)	Si(1)–O(1)–Li(1′)	136.0(2)
Si(1)–O(2)–Si(2)	127.1(1)		
O(3)–Li(1)–O(1)′	87.8(2)	O(3)–Li(1)–O(4)	111.0(3)
O(3)–Li(1)–O(5)	120.9(3)	O(4)–Li(1)–O(5)	105.9(3)
O(4)–Li(1)–O(1′)	109.3(3)	O(5)–Li(1)–O(1′)	121.0(3)
Li(1)–O(4)–C(25)	120.7(3)	Li(1)–O(4)–C(28)	122.0(3)
Li(1)–O(5)–C(32)	127.8(3)	Li(1)–O(5)–C(29)	121.4(3)

CONCLUSION

These results show that the disiloxide ligand, $[OSiPh_2OSiPh_2O]^{2-}$, can arise from reactions involving $[Ph_2SiO_2]^{2-}$. The $[Ph_2SiO_2]^{2-}$ dianion does bind to copper as originally anticipated. Moreover, by forming the dilithio-heterometallic complex **2**, a copper complex is generated which is suitable for further substitution of the lithium by other metals.

SUPPLEMENTARY MATERIAL

Figures and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, models showing the disordered toluene, and structure factors are available from W.J.E.

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