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Exchange of Cobalt(II) for Copper(II) in a Spirocyclic Metallasiloxane Compound; X-Ray Crystal Structure of the Spirocyclic Copper(II)siloxane $\mathrm{Cu(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Lipy_2)_2}$ (py = pyridine)

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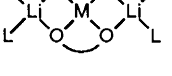
Treatment of the spirocyclic cobalt compound $\mathrm{Co(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Litmeda)_2}$ (tmeda = tetramethylethylenediamine) with $CuCl_2$ and pyridine afforded the analogous copper compound $\mathrm{Cu(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Lipy_2)_2}$ **1** which has been characterised by X-ray crystallography.

The first spirocyclic copper(II)siloxane compound $\mathrm{Cu(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Lipy_2)_2}$ **1**, has been synthesised in an exchange reaction when toluene solutions of the related divalent cobalt compound $\mathrm{Co(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Litmeda)_2}$ were treated with $CuCl_2$ and pyridine. Compound **1** was also formed from $CuCl_2$ and $\mathrm{Ph_4Si_2O(OLi)_2}$ with LiCl elimination and has been characterised by single crystal X-ray studies.

In the course of our work directed towards the synthesis of six-membered cyclic metallasiloxanes, we have observed the lithium-bridged spirocyclic structure **A** for a number of divalent first-row transition metals and reported on the cobalt compounds.[1] These compounds are apparently kinetically stable, in contrast to products obtained from preparations of some simple monocyclic six-membered metallasiloxanes.[2] The title copper compound was formed when the related $\mathrm{Co^{II}}$ species was treated with $CuCl_2$ in tetrahydrofuran (thf), and toluene solutions of the products subsequently treated with pyridine, eqn. (1). The azure-blue moisture sensitive solid was recrystallised from hot toluene. Compound **1** was also obtained when toluene solutions of the product from a standard salt elimination reaction carried out in thf, eqn. (1), were treated with pyridine.

$$\begin{tikzcd} \mathrm{A + CuCl_2} \arrow[r, "\text{pyridine}", "(25\%)"'] & \mathbf{1}\ (\text{m.p.} = 199\text{–}202\,^\circ\mathrm{C}) \quad (1) \\ (\mathrm{M = Co, L = tmeda}) & \\ & \mathrm{2Ph_4Si_2O(OLi)_2 + CuCl_2} \arrow[uu, "(53\%)"', "\text{pyridine}\ -2\mathrm{LiCl}"] \end{tikzcd}$$

The replacement of cobalt by copper, eqn. (1), follows the expected (Irving Williams) thermodynamic stability for the complexes but this is the first example of an Irving Williams-type exchange reaction involving a cyclic metallasiloxane. The observation suggests that the lithium bridged spirocyclic metallasiloxane compounds **A** are labile in solution. It is interesting to note that this lability does not promote siloxane chain expansion despite the nucleophilicity of the chelating oxygens and the strain in the six-membered rings. The isomorphous substitution of Si and Al in zeolite frameworks by elements such as B, P, Ge and Ga has received much attention.[3] Our observation suggests that it may be possible to study a wide range of similar isomorphous substitutions in metallasiloxanes and part of our future work will be directed to this end.



A

L = py, thf, tmeda

$\mathrm{OSiPh_2OSiPh_2O}$ = O‿O

Only one other copper(II) siloxide namely $\mathrm{Cu[OSi(OCMe_3)_3]_2py_2}$ has been structurally characterised.[4] It is noteworthy that products from the reaction between disodium

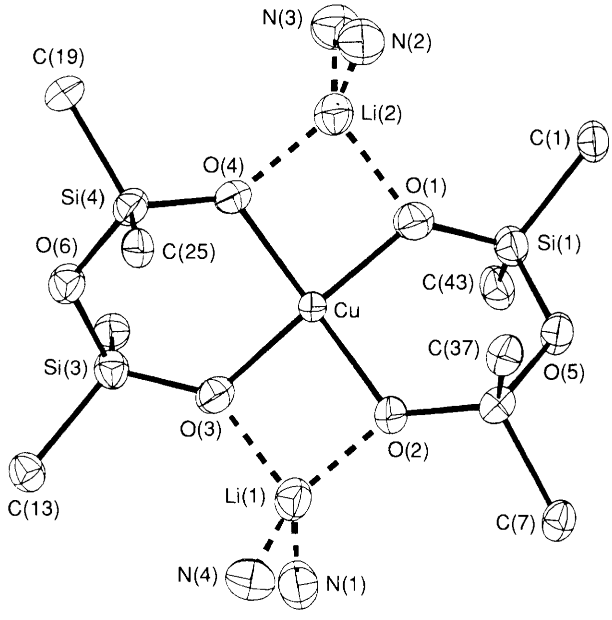


Fig. 1 The X-ray crystal structure of $\mathrm{Cu(OSiPh_2OSiPh_2O)_2\text{-}\mu\text{-}(Lipy_2)_2}$ **1** (phenyl and pyridine groups omitted for clarity). Selected bond lengths (Å) and angles (°) are: Cu–O(1) 1.896(8), Cu–O(2) 1.935(8), Cu–O(3) 1.903(8), Cu–O(4) 1.944(8), Si–O(Cu)av 1.619(9), Si–O(Si)av 1.640(9); O(1)–Cu–O(2) 95.6(4), O(1)–Cu–O(4) 87.1(3), O(2)–Cu–O(3) 86.0(4), O(1)–Cu–O(3) 162.3(3), O(3)–Cu–O(4) 96.7(4), O(4)–Cu–O(2) 162.6(3), Si–O–Si(av) 123.7(5), Si–O–Cu(av) 123.7(5), O–Si–O(av) 110.3.

diphenylsilanediolate $Ph_2Si(ONa)_2$ and $CuCl_2$ were reported to decompose rapidly to copper(II) oxide and cyclooctaphenyltetrasiloxane.[5]

The structure of compound **1** is shown in Fig. 1 along with some pertinent bond lengths and angles.† The coordination geometry may be described as distorted square planar (there are no close intermolecular contacts). The *cis*-O–Cu–O angles range from 86.0(4)–96.7(4)° while the *trans*-O–Cu–O angles are around 162°. The Cu–O distances [1.896(8)–1.944(8) Å] are longer than those in the related alkoxysiloxide compound $Cu[OSi(OCMe_3)_3]_2py_2$ [1.835(6)–1.861(6) Å] but similar to those in other systems with CuO_4 chromophores *e.g.* $Ca[CuSi_4O_{10}]$[6] or $[Cu(3\text{-Meacac})_2]$,[7] (Hacac = pentane-2,4-dione). The small angles at the bridging oxygens [123.4(5) and 123.9(5)° for Si–O–Si and 123.7(5)° for Si–O–Cu_{av}] suggest some strain in the six-membered ring. The Si–O–Si angles are considerably smaller than previously observed in compounds with six-membered metallasiloxane rings.[1,8] While the Si–O distances [1.604(7)–1.643(7) Å] are within ranges previously reported[1,8] the Si–O(Cu) distances are generally shorter than the Si–O(Si).

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† *Crystal data* for **1**: $C_{68}H_{60}O_6N_4Si_4Li_2Cu$, $M = 1219.018$, monoclinic, $a = 17.119(1)$, $b = 17.971(5)$, $c = 20.721(6)$ Å, $\beta = 91.31(3)°$, $U = 6373.06$ Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.27$ g cm^{-3}; λ(Mo-Kα) = 0.71069 Å, $\mu = 4.43$ cm^{-1} $F(000) = 2540.0$. X-Ray measurements were made on a crystal sealed in a glass capillary under nitrogen using an Enraf-Nonius FAST TV area detector and graphite monochromated Mo-Kα radiation. Intensity data corresponding to one hemisphere of reciprocal space were recorded using two ω scan ranges of 100° with a phi shift of 90° (to achieve > 180° in total) at $\chi = 0°$, followed by two further ω rotations of 70° with a phi shift of 90° at $\chi = 90°$, to record the missing cusp data, with a swing angle of 18.0° and a crystal to detector distance of 45.6 mm which yielded all possible reflections to θ_{max} of 22.4°. Of the reflections predicted and scanned, 18340 satisfied the conditions for acceptable measurement and were merged to give 11483 unique data of which 3340 were considered to be observed ($F > 3\sigma F_o$) and corrected for absorption. The structure was solved by standard heavy atom procedures and refined by full-matrix least-squares. The phenyl rings were treated as rigid hexagons (C–C 1.395 Å, C–C–C 120°), with hydrogen atoms included at a fixed distance (C–H 0.96 Å). Final $R = 0.057$, $R_G = 0.061$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.