# Mixed Metal Spirocyclic Metallasiloxanes. Crystal Structure of the Pyridinolithium{bis(cyclodisiloxanediolato)bis(pyridino)cobalt}pyridinomanganese chloride compound $[(\mathrm{Py_2Li})\text{-}\mu\text{-}\{(\overline{\mathrm{Co(OSiPh_2OSiPh_2O}})_2\cdot 2\mathrm{Py}\}\text{-}\mu\text{-}\mathrm{MnClPy}]$

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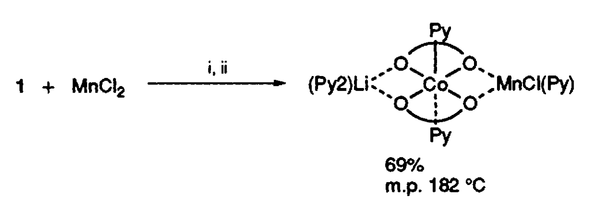
Treatment of a solution of the cobalt compound $[\mathrm{Co(OSiPh_2OSiPh_2O)_2}\text{-}\mu\text{-}(\mathrm{LiTHF_2})_2]$ **1** with manganese(II) chloride affords, after addition of pyridine, the first mixed transition metal metallasiloxane compound $[(\mathrm{Py_2Li})\text{-}\mu\text{-}(\overline{\mathrm{Co(OSiPh_2OSiPh_2O}})_2\cdot\text{-}2\mathrm{Py})\text{-}\mu\text{-}\mathrm{MnClPy}]$ **2**; the results of single crystal X-ray diffraction and magnetochemical studies are reported, although disorder of the solution introduces some ambiguity into the data.

We have reported recently the substitutional lability of the spiro cobalt ion in the compound **1** in the presence of $\mathrm{CuCl_2}$.[1] The stability of the siloxane framework in the face of this lability was surprising especially in view of our observation of siloxane rearrangement in attempted syntheses of related spirocyclic dianionic compounds with discrete uncomplexed anions.[2]

We report here further evidence of the unusual kinetic stability towards rearrangement of metal-bridged spirocyclic compounds of type **1**, demonstrated by substitutional lability of the bridging lithium cations. The title mixed-metal compound was formed as turquoise air-sensitive crystals when solutions of the cobalt compound **1** in tetrahydrofuran, THF, were treated with $\mathrm{MnCl_2}$, and toluene solutions of the products treated subsequently with pyridine (Py); see Scheme 1. The substitution reaction takes place at a bridging lithium site in **1** as expected, leading to the first example of a crystallographically characterised mixed transition metal metallasiloxane compound. We have reported previously a similar homodinuclear compound $[(Py_2Li)\text{-}\mu\text{-}\{\overline{Co(OSiPh_2OSiPh_2O})_2\cdot Py\}\text{-}\mu\text{-}CoClPy]$, **3**, containing two cobalt ions.[3] Compounds **2** and **3**, however, adopt different stereochemistry at the spiro cobalt sites. Feher *et al.* have reported the synthesis, structures and magnetochemistry of a series of solid solutions of polyhedral oligometallasilsesquioxane dimers but did not structurally characterise any heterodinuclear species.[4]

The structure of **2** is shown in Fig. 1 along with selected bond lengths and angles. The geometry at the spiro cobalt is roughly octahedral with the two six-membered cobaltasiloxane rings approximately coplanar. The fifth and sixth axial coordination sites are occupied by pyridine. The manganese chloride and lithium groups bridge opposite edges of the central octahedron and lie almost in the equatorial plane. The crystallographic solution in fact allows for three possible molecules $[(Py_2Li)\text{-}\mu\text{-}\overline{Co(OSiPh_2OSiPh_2O})_2Py_2\text{-}\mu\text{-}MnClPy]$, $[\overline{Co(OSiPh_2OSiPh_2O})_2Py_2\text{-}\mu\text{-}(LiPy_2)_2]$ and $[\overline{Co(OSiPh_2OSiPh_2O})]_2\cdot Py_2\text{-}\mu\text{-}(MnClPy)_2]$. We have isolated previously the bislithium bridged compound from toluene/pyridine solutions and found a tetrahedral cobalt coordination environment. All attempts to generate the bismanganese chloride bridged compound resulted in rearrangement with large amounts of cyclic trisiloxane being formed. These chemical observations support the assigned structure.



**2**

**Scheme 1** *Reagents*: i, THF; ii, toluene/pyridine

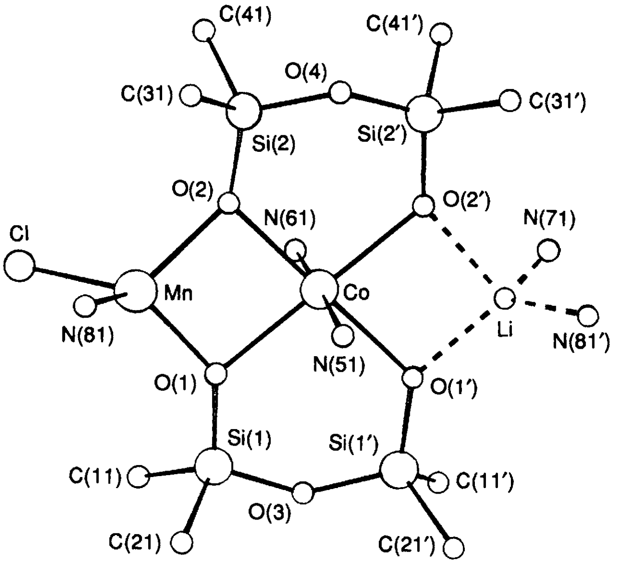


**Fig. 1** Structure of $C_{73}H_{65}ClCoLiMnN_5O_6Si_4$ (phenyl and pyridine atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Mn/Li–O(1) 1.966(9), Mn/Li–O(2) 2.07(1), Mn/Li–Cl 2.25(1), Mn/Li–N(71) 2.14(2), Mn/Li–N(81) 1.95(1), Co–O(1) 2.167(8), Co–O(2) 2.17(1), Co–N(51) 2.39(1), Co–N(61) 2.43(2), Si(1)–O(1) 1.604(8), Si(1)–O(3) 1.628(6), Si(1)–C(11) 1.90(1), Si(1)–C(21) 1.91(1), Si(2)–O(2) 1.593(9), Si(2)–O(4) 1.633(7), Si(2)–C(31) 1.90(1), Si(2)–C(41) 1.88(1); O(1)–Mn/Li–O(2) 89.2(4), O(1)–Mn/Li–Cl 118.5(4), O(1)–Mn/Li–N(71) 112.7(7), O(1)–Mn/Li–N(81) 120.9(4), O(2)–Mn/Li–Cl 118.4(4), O(2)–Mn/Li–N(71) 100.4(7), O(2)–Mn/Li–N(81) 111.7(4), Cl–Mn/Li–N(81) 99.4(4), N(71)–Mn/Li–N(81) 116.3(6), O(1)–Co–O(1)* 99.2(4), O(1)–Co–O(2) 81.6(3), O(1)–Co–O(2)* 177.6(4), O(1)–Co–N(51) 87.1(3), O(1)–Co–N(61) 91.0(3), O(2)–Co–O(2)* 97.5(5), O(2)–Co–N(51) 90.7(3), O(2)–Co–N(61) 91.2(3), N(51)–Co–N(61) 177.1(6), O(1)–Si(1)–O(3) 110.6(6), O(1)–Si(1)–C(11) 111.5(6), O(1)–Si(1)–C(21) 110.5(5), O(3)–Si(1)–C(11) 107.5(6), O(3)–Si(1)–C(21) 108.2(6), C(11)–Si(1)–C(21) 108.4(6), O(2)–Si(2)–O(4) 111.8(6), O(2)–Si(2)–C(31) 110.4(6), O(2)–Si(2)–C(41) 112.5(6), O(4)–Si(2)–C(31) 106.4(6), O(4)–Si(2)–C(41) 108.3(7), C(31)–Si(2)–C(41) 107.1(6), Mn/Li–O(1)–Co 96.1(3). Mn/Li–O(1)–Si(1) 137.2(6), Co–O(1)–Si(1) 126.5(5), Mn/Li–O(2)–Co 93.1(3), Mn/Li–O(2)–Si(2) 139.3(7), Co–O(2)–Si(2) 126.8(6), Si(1)–O(3)–Si(1)* 144.7(8), Si(2)–O(4)–Si(2)* 135.1(9); where * indicates atoms related by centre of symmetry.

The geometry at cobalt in **2**† contrasts with that observed in the related cobalt chloride bridged analogue **3** in which there is a large (55°) ring-twist angle and approximate square-pyramidal geometry at the central cobalt atom. The apparent increased Lewis acidity at the spiro cobalt in the manganese chloride bridged compound **2** implies a more electron-deficient cobalt metal site than in **3**. This may be attributed to more extensive delocalisation in the bridging Mn–O bonds compared with the bridging Co–O bonds in the related complex **3**. Variable-temperature magnetochemical studies of the two compounds were carried out the liquid nitrogen regime. While compound **2** shows distinct antiferromagnetic behaviour this is not the case for **3** and this suggests greater overlap of magnetic orbitals in **2**.

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† *Crystal data* for compound **2**, $[C_{73}H_{85}ClLiMnN_5O_8Si_4]$: $M$ = 1376.96, orthorhombic, space group *Pnma*, $a$ = 21.738(3), $b$ = 23.614(8), $c$ = 13.677(2) Å, $Z$ = 4, $D_c$ = 1.303 g cm$^{-3}$, $F(000)$ = 2856, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$ = 4.38 cm$^{-1}$, 298 K. Data were collected on a capillary-mounted crystal sealed under nitrogen with an Enraf-Nonius FAST TV area detector using the method described previously.[5] 24 529 reflections were recorded corresponding to one hemisphere of data, giving 5079 unique reflections of which 2293 with $I > 6\sigma(I)$ were used in the refinement. The central core of the molecule was found by direct methods using SHELX-87[6] with difference Fourier techniques used to locate the remaining atoms. Structure refinement was carried out using SHELX-76[7]. Initial refinement was in the non-centrosymmetric space group $Pn2_1a$ but failed to yield a satisfactory anisotropic model. The only solution that did lead to a satisfactory refinement was in the centrosymmetric space group *Pnma*, using an averaged 'centrosymmetric' model for the molecule. Mn and Li atoms were fixed at half occupancy of a single averaged site, with Cl and the atoms in one of the Li coordinated pyridine rings also fixed at half occupancy. Data were corrected for absorption using DIFFABS.[8] Anisotropic thermal parameters were applied successfully to all atoms. Phenyl and pyridine rings were treated as rigid hexagons. Hydrogen atoms were not located. Refinement terminated with $R$ = 8.95%, $R_G$ = 10.07%.

Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.