Preparation and X-Ray Structure of $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}O)]_2$, a Rare 1,3-Cyclodigermoxane*

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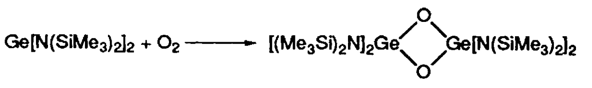
Exposure of the monomeric germanium silylamide $Ge[N(SiMe_3)_2]_2$ to molecular oxygen generates the unusual crystalline digermoxane $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}O)]_2$, characterised by NMR spectroscopy and X-ray crystallographic data [Ge–O(av.) 1.805(9) Å; O–Ge–O(av.) 87.5(4), Ge–O–Ge(av.) 92.5(4)°].

1,3-Cyclodimetalloxanes of the Group 14 elements $[MX_2(\mu\text{-}O)]_2$ are extremely rare and are restricted to at least one of the groups X being hydrocarbyl. The sole structurally authenticated 1,3-cyclodistannoxane is $[Sn(CHR_2)_2(\mu\text{-}O)]_2$ ($R = SiMe_3$),[1] and the only hitherto known germanium and silicon analogues were $[GeR'_2(\mu\text{-}O)]_2$ [$R' = C_6H_3Et_2$-2,6 or $C_6H_3Pr^i_2$-2,6],[2] and $[Si(R''R''')_2(\mu\text{-}O)]_2$ ($R'' = R''' = C_6H_2Me_3$-2,4,6 or Bu^t; or $R'',R''' = C_6H_2Me_3$-2,4,6, NR_2 or $C_6H_2Me_3$-2,4,6, Bu^t),[3] respectively; with less hindered groups X, oligomers or polymers are found. Each of the cyclodimetalloxanes was made by oxidation of a crystalline $X_2M{=}MX_2$ precursor. For compounds having five-co-ordinate Ge or Sn, four-membered $\overline{M{-}O{-}M{-}O}$ rings are known.[4]

Whereas the stannylene $Sn(NR_2)_2$ ($R = SiMe_3$) was shown to react with molecular oxygen to yield the remarkable bis(1,2-μ-peroxo)-bridged tin(IV) complex $[Sn(NR_2)_2(\mu\text{-}O_2)]_2$,[5] we now report that a similar experiment with the isoleptic germanium compound $Ge(NR_2)_2$ proceeded differently. Thus, a pentane solution of orange $Ge(NR_2)_2$ (ref. 6) was rapidly decolourised by molecular oxygen and, surprisingly, the product was the colourless, crystalline 1,3-cyclodigermoxane **1**, obtained in virtually quantitative yield, equation (1).†



$$Ge[N(SiMe_3)_2]_2 + O_2 \longrightarrow [(Me_3Si)_2N]_2Ge(\mu\text{-}O)_2Ge[N(SiMe_3)_2]_2 \qquad (1)$$

1

Some comparative X-ray data for (*i*) $Ge[N(SiMe_3)_2]_2$,[7] $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}Te)]_2$[8] and **1** are in Table 1 and (*ii*) the 1,3-cyclodimetalloxanes $[MX_2(\mu\text{-}O)]_2$ (M = Si, Ge or Sn) (together with M–M bond lengths taken from the bulk metal, M_∞) are in Table 2.

X-Ray crystallography‡ (Fig. 1) reveals that there are two identical molecules of **1** in the asymmetric unit. The Ge_2O_2 ring in **1** is planar and approximately square, the average O–Ge–O and Ge–O–Ge angles are 87.5(4) and 92.5(4)°, respectively. These match very closely the values in $[Ge(C_6H_3Et_2\text{-}2,6)_2(\mu\text{-}O)]_2$ **2** of 87.6(1) and 92.2(1)°, respectively, which, however, has the Ge_2O_2 ring slightly puckered,[2] as are the Si_2O_2 rings in the cyclodisiloxanes.[3] The average Ge–O bond length in **1** is only marginally shorter [1.805(9) Å] than in **2**, 1.817(2) Å, and may be compared with the 1.741(5) Å in $[Ge(CF_3)_2(\mu\text{-}O)]_\infty$.[10] In both **1** and **2** the transannular Ge ··· Ge separation [2.608 and 2.617(1) Å in **1** and **2**, respectively] is less than 10% longer than the normal Ge–Ge bond length [*e.g.* 2.445 Å in $(Ge)_\infty$], but is much shorter than twice the van der Waals Ge^{4+} radius (4.30 Å). Similar effects have been noticed in the other 1,3-cyclodimetalloxanes of the Group 14 elements (Table 2); the

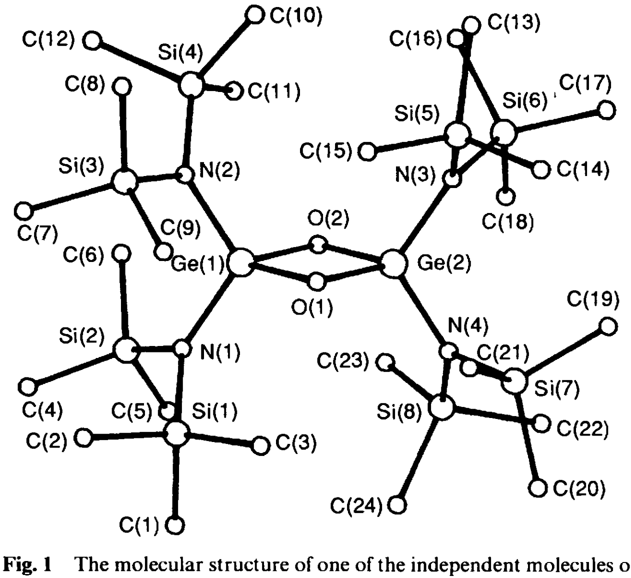


Fig. 1 The molecular structure of one of the independent molecules of $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}O)]_2$ **1** and atom numbering scheme

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* No reprints available.

† Preparation of compound **1**. An orange solution of $Ge[N(SiMe_3)_2]_2$[6] (4.06 g, 10.3 mmol) in pentane (30 cm^3) was shaken in an atmosphere of dioxygen gas until it was completely decolourised. Volatiles were removed from the colourless solution *in vacuo* affording a white solid residue of crude **1** (4.3 g, 100%). Colourless crystals of the 1,3-cyclodigermoxane **1**, m.p. 140 °C (Found: C, 35.3; H, 8.60. $C_{24}H_{72}Ge_2N_4O_2Si_8$ requires C, 35.2; H, 8.80%) were obtained by recrystallisation from diethyl ether at −30 °C. The following spectroscopic data in [$^2H_8$]toluene at 303 K were obtained: ^1H, δ 0.37; $^{13}C\text{-}\{^1H\}$, δ 6.31 (s); $^{29}Si\text{-}\{^1H\}$, δ 5.46 (s).

‡ Crystal data. $C_{24}H_{72}Ge_2N_4O_2Si_8$, $M = 818.7$, orthorhombic, spac group *Pbcn* (no. 60), $a = 27.687(4)$, $b = 18.105(9)$, $c = 35.742(11)$ Å, $U = 17\,916.3$ Å^3, $Z = 16$, $D_c = 1.21$ g cm^{-3}, $F(000) = 6976$, $\mu(\text{Mo-K}\alpha) = 15.6$ cm^{-1}, $T = 293$ K, specimen 0.3 × 0.3 × 0.2 mm, 9961 unique reflections for $2 < \theta < 20°$, 3592 reflections with $|F^2| > 2\sigma(F^2)$ used in the refinement with weights of $w = \sigma^{-2}(F)$; $R = 0.056$, $R' = 0.056$. Enraf-Nonius CAD-4 diffractometer; absorption correction; structural solution by heavy-atom methods (SHELXS 86).[9] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Comparative selected X-ray structural data for $Ge(NR_2)_2$ and $[Ge(NR_2)_2(\mu\text{-}E)]_2$ ($R = SiMe_3$, $E = O$ or Te)

Compound	Ge–N/Å	N–Ge–N′/°	Ge–E–Ge′/°	α^a	β^b	Ref.
$Ge(NR_2)_2$	1.878(5), 1.873(5)	107.1(2)	—	12.3	120.6(4)	7
$[Ge(NR_2)_2(\mu\text{-}Te)]_2$	1.869(10), 1.873(12)	108.1(5)	85.58(6)	17.5	114.5(9)	8
	1.867(12), 1.858(13)	109.0(6)	85.59(6)		118.0(9)	
1 $[Ge(NR_2)_2(\mu\text{-}O)]_2$	1.839(11), 1.819(10)	114.8(5)	93.7(4)	10.2	116.7(7)	This work
(molecule 1)	1.817(10), 1.830(10)	114.7(5)	92.7(4)		119.2(4)	
1 $[Ge(NR_2)_2(\mu\text{-}O)]_2$	1.817(10), 1.820(11)	115.3(5)	92.2(4)	10.0	117.6(6)	This work
(molecule 2)	1.804(10), 1.836(10)	115.3(5)	91.5(4)			

[a] Angle α is the difference between the greatest and smallest Ge–N–Si angle. [b] Angle β is the mean value of the Si–N–Si angles.

Table 2 Transannular separations and mean O–M–O angles in 1,3-cyclodimetalloxanes $[MX_2(\mu\text{-}O)]_2$ (M = Si, Ge or Sn) and M–M bond lengths in $(M)_x$

Compound	M ··· M/Å	O ··· O/Å	M–M in $(M)_\infty$/Å	O–M–O(av.)/°	Dihedral angle between MMO planes/°	Ref.
$[Si(C_6H_2Me_3\text{-}2,4,6)_2(\mu\text{-}O)]_2$	2.306(3)	2.460(8)	2.35	94.49(13)	6	3(*a*)
trans-$[Si(C_6H_2Me_3\text{-}2,4,6)Bu^t(\mu\text{-}O)]_2$	2.396(11)	2.349(3)	2.35	88.87(7)	0	3(*a*)
cis-$[Si(C_6H_2Me_3\text{-}2,4,6)\{N(SiMe_3)_2\}(\mu\text{-}O)]_2$	2.349(1)	2.358(4)	2.35	90.2(1), 89.8(1)	10	3(*a*)
$[SiBu^t{}_2(\mu\text{-}O)]_2$	2.453	*	2.35	*	*	3(*b*)
1 $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}O)]_2$ (molecule 1)	2.608(2)	2.463(13)	2.45	86.7(5)	0	This work
(molecule 2)	2.606(2)	2.524(13)		88.1(5)		
2 $[Ge(C_6H_3Et_2\text{-}2,6)_2(\mu\text{-}O)]_2$	2.617(1)	2.564	2.45	87.6(1)	8.5	2
$[Sn\{CH(SiMe_3)_2\}_2(\mu\text{-}O)]_2$	2.94	2.55	2.79	82.5(6)	0	1

* Not listed; coordinates not available.

short transannular M ··· M and O ··· O contacts have been attributed to geometric constraints rather than unusual bonding features.[11]

The Ge–N bond lengths in **1** vary from 1.804(10) to 1.839(11) Å, being significantly shorter than in $Ge(NR_2)_2$ or $[Ge(NR_2)_2(\mu\text{-}Te)]_2$. The N–Si bond lengths in **1** range from 1.75(1) to 1.78(1) Å. The N–Ge–N bond angle has opened out from 107.1(2)° in crystalline $Ge(NR_2)_2$ to an average of 115.0° in the ring compound **1**. The geometry at the N atoms is planar.

The reactivity of compound **1** is of interest, because its NR_2 groups, unlike hydrocarbyls, are susceptible to ready nucleophilic displacement; such reactions are being investigated.

Acknowledgements

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