Compounds of Germanium and Tin, 22[◇]

Reactions of a Silylene with a Germylene and a Stannylene: Formation of a Digermene with an Unusual Arrangement of the Substituents and of a Stannane

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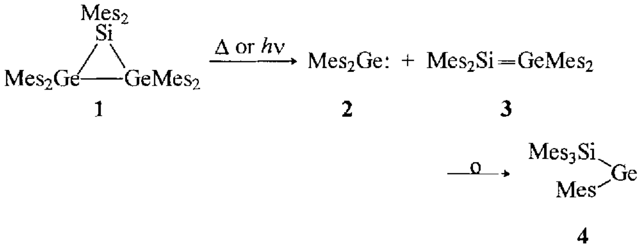
The reaction of the diaminosilylene :Si(*t*BuNCH$_2$CH$_2$N*t*Bu) (**5**) with the diaminogermylene :Ge(*t*BuNCH$_2$CH$_2$N*t*Bu) is thought to proceed via a germasilene → silylgermylene rearrangement and dimerisation to furnish the (Z)-1,2-diamino-1,2-disilyldigermene (Z)-**9**. The X-ray structure analysis of (Z)-**9** reveals a long Ge=Ge bond length of 245 pm and a large *trans*-bent angle of 42°. Air-oxidation of (Z)-**9** takes place with retention of configuration at the germanium atoms to provide the corresponding substituted (Z)-2,4-digerma-1,3-dioxetane (Z)-**10**. Treatment of **5** with the stannylene :Sn[N(SiMe$_3$)$_2$]$_2$ gives, as a final product, the hydridodisilylstannane **12**. The structures of (Z)-**10** and **12** were also determined by X-ray crystallography.

In contrast to the numerous compounds containing homonuclear Si=Si,[2], Ge=Ge,[3] and Sn=Sn[3] double bonds which are currently known, stable molecules with heteronuclear multiple bonds between these elements have yet to be isolated. In a series of papers, Baines et al. have reported on the thermolysis and photolysis of the siladigermirane **1**, which lead regioselectively to the germylene **2** and the germasilene **3**. The latter species rearranges relatively rapidly to furnish the silylgermylene **4**. The existence of the compounds **2**, **3**, and **4** in the respective reaction mixtures was confirmed by the isolation of products from numerous trapping reactions.[4–7]



Mes = 2,4,6-Me$_3$C$_6$H$_2$

Theoretical calculations support this observation on the ease of isomerisation of the germasilene to the silylgermylene.[8][9] Since the mesityl groups in **3** apparently exhibit a large tendency for 1,2-shifts, Baines et al. prepared a derivative of **1** with *tert*-butyl groups in place of the mesityl groups at the silicon atom. Photolysis of this compound, again regioselectively, furnished both a germasilene and **2**; both products were identified by trapping reactions. In contrast to compound **3**, however, the germasilene in question appears to decompose into *t*Bu$_2$Si: and Mes$_2$Ge upon lengthy photolysis. The occurrence of these species seems reasonable on the basis of the products obtained from their insertion reactions into the Si–H bond of Et$_3$SiH.[10] Recently, the formation of the first stannagermene by elimination of HF from a stannylgermane, its characterisation by low temperature NMR spectroscopy, and some subsequent reactions were all reported.[11]

Reactions between various electron sextet moieties, which are now known for all elements of group 14, offer an alternative approach to the formation of heteronuclear double bonds between the heavier elements of group 14. However, in the majority of cases no reaction could be observed. Only the action of a cyclic silylene on both a germylene and a stannylene led to the unusual reaction sequence; these reactions are reported in this paper.

Results and Discussion

The first reaction of this type investigated involved the action of the cyclic diaminosilylene **5**[12][13] with the analogous substituted germylene **6**.[14] On account of the thermal lability of **5**, as well as that of the resulting product, this and all subsequent operations were carried out at a low temperature. On mixing the colourless solutions of **5** and **6** in *n*-hexane a deep-red coloration appeared, indicative of a rapid reaction between these two components. A red pow-

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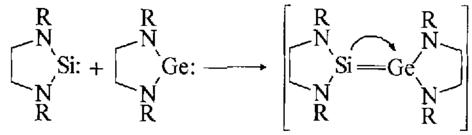
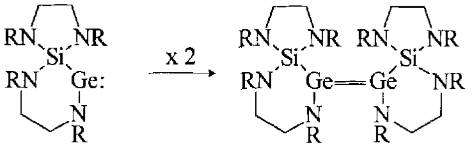
[◇] Part 21: Ref.[1].

der was isolated which decomposed slowly at room temp. in the solid state but rapidly when in solution.



5 **6** **7**



8 (*Z*)-**9**

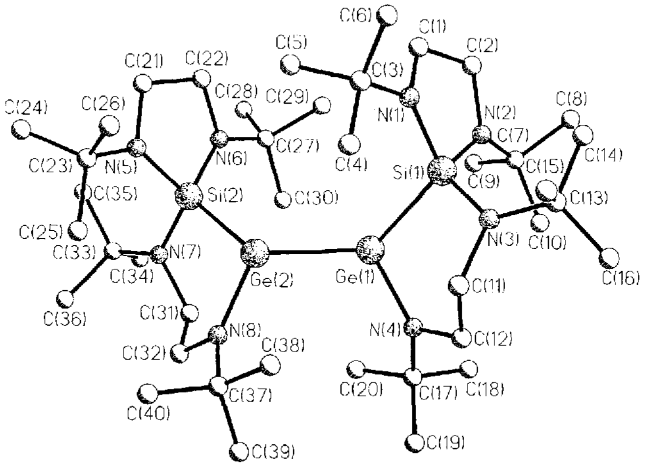
R = *t*Bu

The NMR spectra at first provided little information about the constitution of the product formed. The ^{29}Si-NMR spectrum only showed a singlet at $\delta = 22.4$, indicating that the formation of a germasilene of the type **3** could be excluded, since such a compound would give rise to a markedly more strongly deshielded signal. The structure of the reaction product was finally resolved by X-ray crystallography (Figure 1a, b), which also revealed a number of unexpected details.

The reaction of the two carbene homologues **5** and **6** has, therefore, led to the digermene (*Z*)-**9**, instead of the expected germasilene. The structure of **9** bears almost no resemblance to that of any other previously prepared digermene. The Ge=Ge bond length of 245 pm is considerably longer than for that of the known tetraalkyl- and tetraaryldigermenes[1][15][16][17], and is closer to the value for a normal Ge–Ge single bond. Equally unusual are the *trans*-bent angles of 41.3° and 42.3° between, respectively, the planes Si(1)–N(4)–Ge(1) and Si(2)–N(8)–Ge(2), and the Ge(1)–Ge(2) vector, which exceed all previously observed bending angles (6°–36°), but which lie in the range of the theoretically calculated *trans*-bent angles[5][18][19][20][21] (35–47°) for the parent compound $H_2Ge{=}GeH_2$.

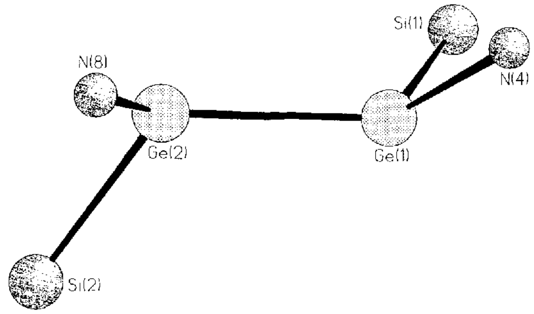
The values of bond length and angle observed here are even more surprising in the light of those for the recently prepared, persilylated digermenes, which have a short Ge=Ge bond length and an almost planar orientation of the silyl substituents about the Ge=Ge double bond.[22] A possible explanation, for both the magnitude of the Ge=Ge bond length and the pronounced *anti*-pyramidalisation in (*Z*)-**9**, may involve the interplay between the amino and silyl groups at the germanium atoms. In agreement with theoretical calculations,[23] diaminosilylenes, and diaminogermylenes of the types **5** and **6** do not exhibit any tendency to dimerisation despite their electron deficient nature, whereas the presence of silyl substituents apparently leads to the formation of stable digermenes.[22] As a compromise between these two opposing tendencies (*Z*)-**9**, like the other digermenes, seems to experience a donor-acceptor interaction between the doubly occupied 4s orbital of the one germanium atom, and the empty 4p orbital of the other germanium atom; however, this interaction is considerably less pronounced than is the case for other digermenes whose structures have been determined.

Figure 1a. Molecular structure of (*Z*)-**9** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Ge(1)–Ge(2) 245.4(2), Ge(1)–Si(1) 243.8(2), Ge(1)–N(4) 186.3(5), Ge(2)–Si(2) 244.5(2), Ge(2)–N(8) 186.2(5), Ge(2)–Ge(1)–Si(1) 120.9(1), Ge(2)–Ge(1)–N(4) 114.9(2), Si(1)–Ge(1)–N(4) 102.9(2), Ge(1)–Ge(2)–Si(2) 120.0(1), Ge(1)–Ge(2)–N(8) 115.6(2), Si(2)–Ge(2)–N(8) 102.0(2).

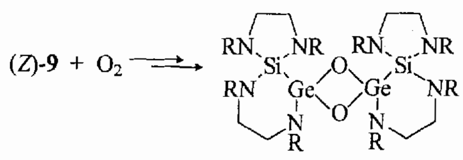
Figure 1b. Side view of the $Ge_2N_2Si_2$ framework of (*Z*)-**9**



Unexplained is the preference for the sterically overcrowded (*Z*) form over the, presumably less sterically stressed, (*E*) configuration. This type of substituent arrangement may also be responsible for the fact that the molecule (*Z*)-**9** exhibits an average torsion angle of 22.3° in spite of the large Ge=Ge bond length; thus reducing the interactions between the substituents. No less surprising is the fact that four molecules of (*Z*)-**9** cocrystallise with one molecule each of silylene **5** and germylene **6**, with the electron sextet moieties statistically oriented like solvent molecules between the digermene molecules. The presence of **5** in the crystal is, presumably, also responsible for the thermal lability of (*Z*)-**9**.

At present, we can only speculate on the route of formation of the digermene (*Z*)-**9**. It is feasible that, analagous to the observations of Baines et al.[4–7] the adduct **7** is first formed from **5** and **6**, and that a subsequent germasilene → silylgermylene rearrangement furnishes **8**, which then undergoes dimerisation to produce the isolated product (*Z*)-**9**.

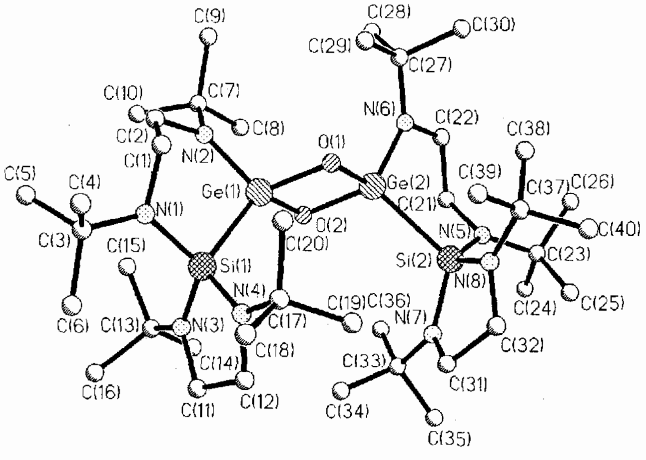
An alternative mechanism would comprise a direct insertion of the silylene **5** into one of the Ge−N bonds of **6**, leading directly to **8** and its dimerisation product (*Z*)-**9**.



(*Z*)-**10**

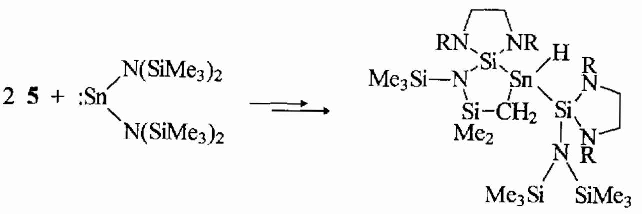
One of the most interesting reaction properties of disilenes and digermenes is their behaviour towards triplet oxygen molecules leading, in both cases, to 1,2-dioxetanes which undergo rapid rearrangement to 1,3-dioxetanes in the case of the disilicon compound[24], or rearrangement only after irradiation at 254 nm in the case of the digermanium compounds.[25] In a comprehensive investigation, West et al. showed that the reaction of 1,2-di-*tert*-butyl-1,2-dimesityldisilene with oxygen first produces a corresponding substituted 3,4-disila-1,2-dioxetane, which then undergoes intramolecular rearrangement, with retention of configuration both in solution and in the crystalline state, to yield the 2,4-disila-1,3-dioxetane.[24] In a similar manner, solutions of (*Z*)-**9** are rapidly decolourised when in contact with dry air at 0 °C, and colourless crystals of a dioxetane can be isolated from the solutions in high yield.

Figure 2. Molecular structure of (*Z*)-**10** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Ge(1)−O(1) 180.4(3), Ge(1)−O(2) 184.9(3), Ge(2)−O(1) 180.4(3), Ge(2)−O(2) 184.4(3), O(1)−Ge(1)−O(2) 86.42(12), O(1)−Ge(2)−O(2) 86.57(12), Ge(1)−O(1)−Ge(2) 93.43(13), Ge(1)−O(2)−Ge(2) 93.55(12).

The X-ray structural analysis of these crystals clearly shows that the reaction with atmospheric oxygen has proceeded with retention of configuration to furnish (*Z*)-**10**. The reaction of $^3O_2$ with (*Z*)-**9** apparently proceeds in an analagous manner to that for the examples[24][25] mentioned above, through the 1,2-dioxetane which is initially formed, which then undergoes spontaneous rearrangement, even at the lower temperature employed in this case, to the 1,3-dioxetane (*Z*)-**10**.



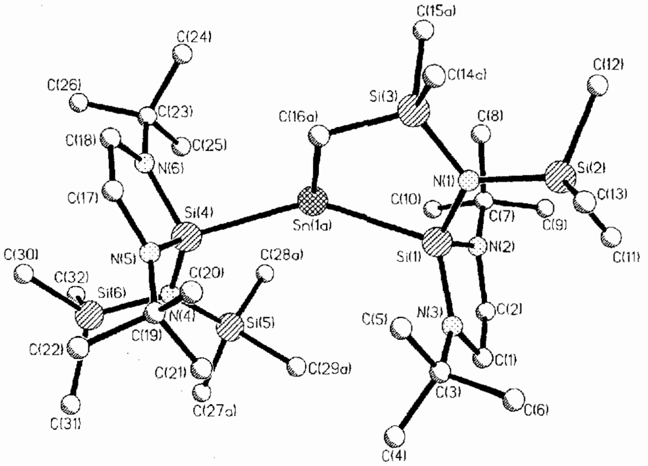
11 **12**

R = *t*Bu

The unexpected formation of a digermene from the reaction of **5** with **6** prompted us to examine the reaction of the silylene **5** with a stannylene. Since we have so far been unable to generate a cyclic stannylene analogue of **5** or **6**, we chose the acyclic diaminostannylene **11**[26] and examined its reaction with **5** at room temp. The solution of the two components in *n*-hexane, which is initially an orange colour, slowly turned black. At first a dark-coloured, crude product was isolated which afforded colourless crystals upon recrystallisation. The lack of colour of the isolated compound, as well as its spectroscopic data, indicated that the product was not a low coordination compound. For example, the ^{29}Si-NMR spectrum showed six signals between $\delta = -32$ and +9, i.e., in the region typical for tetracoordinated silicon atoms. Both ^{1}H-NMR and IR spectra unambiguously demonstrated the presence of an Sn−H bond.

The X-ray crystallographic analysis (Figure 3) revealed that the reaction of **5** with **11** gave rise to the stannane **12**. In spite of its complex structure, the mechanism of formation of **12** should be similar to that for the digermene (*Z*)-**9**. Again, the first step of the reaction sequence could be the formation of a loose adduct between **5** and **11** which then undergoes a stannasilene → silylstannylene rearrange-

Figure 3. Molecular structure of **12** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Sn(1)−Si(1) 262.2(2), Sn(1)−Si(4) 264.1(2), Sn(1)−C(16) 216.9(8), Si(1)−Sn(1)−Si(4) 145.48(5), Si(1)−Sn(1)−C(16) 90.6(2), Si(4)−Sn(1)−C(16) 103.7(2).

ment. A repetition of this process should furnish a disilylstannylene. While the postulated germylene intermediate in the reaction of **5** with **6** is relatively rigid on account of its incorporation in a spirocyclic ring system, the mobile bis(trimethylsilyl)amino groups allow an insertion of the unsaturated tin atom into a C−H bond, with formation of the isolated hydridodisilylstannane **12**. Although the product **12** contains a tetracoordinated tin atom, it is not particularly stable and, for example, decomposes in solution at room temp. with the appearance of a dark colour that is presumed to be due to deposition of tin.

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Experimental Section

All manipulations were performed under dry nitrogen or argon by using Schlenk techniques. Solvents were purified, dried, and distilled under argon. – ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR: Bruker AMX 300 or Bruker AM 300. – UV/Vis: ConSpec with fibre optics. – IR: Bio-Rad FTS-7. – Elemental analyses: Analytische Laboratorien, D-51779 Lindlar, Germany.

Formation of the (Z)-1,2-Diamino-1,2-disilyldigermene (*Z*)-**9**: At 0°C, a solution of 0.6 g (3 mmol) of **5** in 20 ml of *n*-hexane was added to a solution of 0.74 g (3 mmol) of **6** in 20 ml of *n*-hexane. The colour of the mixture changed spontaneously from colourless to deep red. After stirring for 0.5 h at 0°C the solvent was distilled off in vacuo and the residue crystallised at −18°C from a minimum amount of *n*-hexane to furnish 0.70 g (52% yield) of (*Z*)-**9** as a dark red powder, m.p. 55°C (dec.). – ^{1}H NMR ([D$_8$]toluene, 253 K): δ = 1.07 (s, 9 H), 1.08 (s, 9 H), 1.23 (s, 9 H), 1.25 (s, 9 H), 2.56−3.02 (m, 8 H). – ^{13}C NMR ([D$_8$]toluene, 253 K): δ = 30.18, 30.46, 31.23, 31.38, 42.76, 42.94, 47.33, 51.80, 51.93, 52.91, 55.99, 57.56. – ^{29}Si NMR ([D$_8$]toluene, 253 K): δ = 22.39. – UV/Vis: λ_{max} = 475 nm.

Formation of the (Z)-2,4-Diamino-2,4-disilyl-2,4-digerma-1,3-dioxetane (*Z*)-**10**: Treatment of a solution of 0.50 g (5.7 mmol) of (*Z*)-**9** in 40 ml of *n*-hexane with dry air led to an immediate change in the colour from an initial dark red to colourless. The solution was concentrated to a volume of 10 ml and cooled to −18°C to afford 0.47 g (90% yield) of colourless crystals of (*Z*)-**10**, m.p. 174−176°C. – ^{1}H NMR ([D$_8$]toluene, 25°C): δ = 1.23 (s, 9 H), 1.41 (s, 18 H), 1.62 (s, 9 H), 2.97 (s, 4 H), 3.06 (s, 4 H). – ^{13}C NMR ([D$_8$]toluene, 25°C): δ 29.96, 30.53, 31.57, 42.00, 43.83, 49.68, 51.34, 55.33, 57.17. – ^{29}Si NMR ([D$_8$]toluene, 25°C): δ = −28.31. – $C_{40}H_{88}Ge_2N_2O_2Si_2$ (914.58): calcd. C 52.56, H 9.70, N 12.25; found C 52.53, H 9.86, N 12.09.

Formation of the Hydridodisilylstannane **12**: A solution of 3.3 g (0.76 mmol) of **11** in 25 ml of *n*-hexane was added to a solution of 0.75 g (3.8 mmol) of **5** in 25 ml of *n*-hexane, and the mixture was stirred overnight at room temp.. During this time the solution changed from an orange colour to black. The solution was concentrated to a volume of 10 ml and cooled to −18°C. The precipated dark solid was recrystallised from a minimum amount of *n*-hexane to provide 1.3 g (80% yield) of colourless crystals of **12**, m.p. 100−105°C (dec.). – ^{1}H NMR ([D$_8$]toluene, 253 K): δ = 0.12−0.24 ($SiCH_3$, $SiCH_2$, accumulation of signals), 1.02 (s, 9 H), 1.03 (s, 9 H), 1.06 (s, 9 H), 1.09 (s, 9 H), 2.56−2.75 (m, 8 H), 4.05 (dd, 1 H, $^3J_{H,H}$ = 8.3 Hz, SnH). – ^{29}Si NMR ([D$_8$]toluene, 253 K): δ = −31.59, −22.52, 2.17, 2.36, 2.79, 8.56. – ^{119}Sn NMR ([D$_8$]toluene, 273 K): δ = −408 ($^1J_{(119)Sn,H}$ = 1013 Hz). – IR (KBr): $\tilde{\nu}$ = 1736 (SnH) cm^{-1}. – $C_{32}H_{80}N_6Si_6Sn$ (836.25): calcd. C 45.96, H 9.64, N 10.05; found C 47.54, H 10.03, N 8.90. Owing to the thermal lability of **12** no satisfactory elemental analysis could be obtained.

X-ray Structural Analyses of (*Z*)-**9**, (*Z*)-**10**, *and* **12**: Single crystals were grown from saturated solutions in *n*-hexane [(*Z*)-**9**, (*Z*)-**10**] or diethyl ether (**12**). The structures were solved by direct phase determinations using the SHELXS program system and refined by full-matrix least-squares techniques against F^2 [(*Z*)-**10**, **12**] or F with the SHELXL 93[27] or SHELXTL PLUS program systems.

Table 1. Crystallographic data of (*Z*)-**9**, (*Z*)-**10**, and **12**

	4 (*Z*)-**9**·**5**·**6**[a]	(*Z*)-**10**	**12**
Formula	$C_{180}H_{396}Ge_9N_{36}Si_9$	$C_{40}H_{88}Ge_2N_8O_2Si_2$	$C_{32}H_{80}N_2Si_6Sn$
Mol. mass	3971.45	914.58	836.25
Cryst. dimensions [mm]	0.47 × 0.23 × 0.21	0.87 × 0.65 × 0.30	0.76 × 0.27 × 0.23
Cryst. system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a [pm]	1132.3(6)	1003.0(1)	994.4(10)
b [pm]	4689(3)	2004.6(1)	2132.0(1)
c [pm]	1099.8(4)	2494.90(10)	2274.8(2)
β [°]	109.98(4)		102.10(2)
V [× 10^6 pm^3]	5485.2	5016.3	4715.6
Z	1	4	4
$d_{calcd.}$ [g cm^{-3}]	1.203	1.211	1.178
Diffractometer	Siemens P4RA	Siemens STOE AED 2	
Radiation (graphite-monochromated) [pm]	Mo-K_α 71.073	Mo-K_α 71.073	Mo-K_α 71.073
T [K]	150	296(2)	296(2)
μ [mm^{-1}]	1.32	1.285	0.721
Scan method	ω	ω	ω
2θ (max) [°]	54	50	48
No. of unique reflections	11365	4907	7380
No. of observed reflections	6032	4527	5941
Parameters	556	487	434
R [$I > 2\sigma(I)$]	0.062, 0.054 (Rw)	0.032	0.061
$wR2$ (all data)		0.083	0.134

[a] See text.

Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically. The tin atom, as well as the carbon atoms C(14)–C(16) and C(27)–C(29), of **12** are disordered and were refined on two positions with occupancy factors of 0.8 and 0.2. Crystal data and numerical data of the structure determinations are given in Table 1.[28]

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[28] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100 486. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Fax. (internat.) +44 (0)1223/ 336-093. E-mail: deposit@chemcrys.cam.ac.uk.

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