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[30] Crystal data for **1a**: $C_{30}H_{42}Cu_2N_2O_{14} \cdot 1.75\,H_2O \cdot 0.5\,CH_3OH$, $M_r = 837.79$, blue prisms, crystal size $0.28 \times 0.24 \times 0.20$ mm³, monoclinic, space group $P2_1$, $a = 10.3923(3)$, $b = 13.8859(5)$, $c = 25.9903(8)$ Å, $\beta = 101.517(2)°$, $V = 3675.1(2)$ Å³, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.514$ g cm⁻³, $\mu(Mo_{K\alpha}) = 12.33$ cm⁻¹, $F(000) = 1748$; a total of 15126 reflections up to $h(0/14)$, $k(-19/19)$, $l(-25/27)$ in the range $2.30° \leq \Theta \leq 30.52°$ (completeness of data $\Theta_{max} = 78.2\,\%$), of which 14812 were symmetry-independent ($R_{int} = 0.0410$) and 11657 observed with $F_o > 4\sigma(F_o)$, 933 parameters, 1 restraint, $R1_{obs} = 0.081$, $wR^2_{obs} = 0.141$, $R1_{all} = 0.1106$, $wR^2_{all} = 0.1533$, GOF = 1.095, Flack parameter 0.35(1) (racemic twin), max./min. residual electron density $0.646/-0.695$ e Å⁻³. Distances [Å] and angles [°]: Cu(A)···Cu(B) 2.977(1), Cu(A)/Cu(B)−O/N 1.893(5)–1.956(5), Cu(A)−O8(A) 2.382(5); O/N-Cu-O/N 76.1(2)–102.1(2) and 166.6(2)–173.8(2), Cu(C)···Cu(D) 3.020(1), Cu(C)/Cu(D)−O/N 1.918(5), Cu(C)−O(4) 2.674(5), O/N-Cu-O/N 75.9(2)–107.6(2) and 166.7(2)–176.1(2).[31b]

[31] a) Crystal data for **2**: $C_{34}H_{52}Cu_3N_2O_{18}$, $M_r = 967.40$, blue prisms, crystal size $0.32 \times 0.30 \times 0.20$ mm³, monoclinic, space group $P2_1$, $a = 10.0735(3)$, $b = 21.3865(7)$, $c = 10.4135(2)$ Å, $\beta = 110.789(1)°$, $V = 2097.4(1)$ Å³, $T = -90$ °C, $Z = 2$, $\rho_{calcd} = 1.532$ g cm⁻³, $\mu(Mo_{K\alpha}) = 15.82$ cm⁻¹, $F(000) = 1002$; a total of 6973 reflections up to $h(-12/12)$, $k(-20/26)$, $l(-12/13)$ in the region $5.19 \leq \Theta \leq 26.37°$ (completeness of data $\Theta_{max} = 98.7\,\%$), of which 6973 were symmetry-independent ($R_{int} = 0.035$) and 6127 observed with $F_o > 4\sigma(F_o)$; 514 parameters, 1 restraint, $R1_{obs} = 0.039$, $wR^2_{obs} = 0.087$, $R1_{all} = 0.050$, $wR^2_{all} = 0.094$, GOF = 1.029, Flack parameter 0.01(1), max./min. residual electron density $0.257/-0.355$ e Å⁻³. Distances [Å] and angles [°]: Cu(A)···Cu(B) 5.735(3), Cu(A)···Cu(C) 3.248(3), Cu(B)···Cu(C) 3.207(3), Cu−O/N 1.940(4), Cu(A)···O6(B) (symmetry operation for equivalent atoms: $-x$, $0.5 + y$, $-z$) 2.753(4), Cu(B)···O2(A) 2.898(4), Cu(C)−O2(A) 2.586(4), Cu(C)−O2(B) 2.572(4); O1(A)-Cu(A)-N1(A) 95.6(1), O/N-Cu-O/N 73.6(1)–106.9(1) and 152.0(1)–172.3(1). b) 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-129253 (**1a**) and -129254 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[32] General remarks on the kinetic investigations: The measurements were carried out as described in J. Reim, B. Krebs, *J. Chem. Soc. Dalton Trans.* **1997**, 3793–3804. For qualitative testing of the catalytic activities, 10^{-4} M solutions of the copper complexes in methanol were mixed with 50 equivalents of dtcb. The reaction with oxygen was monitored by observing the absorption of the quinone at 400 nm against a solution of the pure complex with the same concentration by means of UV/Vis spectroscopy (VARIAN-Spectrophotometer Cary 5). As reference for the catalytic reaction, a 10^{-4} M solution of copper acetate monohydrate was used, which shows a significant lower activity ($k < 1.5$ h⁻¹). The given rate constants are mean values of three measurements with a discrepancy value of the Lineweaver–Burk plot of $r \geq 0.992$.

Simple Synthesis of a Chlorin–Fullerene Dyad with a Novel Ring-Closure Reaction[**]

Franz-Peter Montforts* and Olaf Kutzki

Amongst the covalent functionalizations of buckminster fullerene C_{60},[1] the linkage to porphyrins has opened the possibility of constructing artificial photosynthetic systems[2] in which there is light-induced transfer of electrons or energy from a porphyrin donor to a fullerene acceptor. Apart from one example in which a derivative of naturally occurring chlorophyll was attached to a fullerene by [2+3] cycloaddition,[3] all known fullerene-based photosynthetic models contain completely unsaturated porphyrins and phthalocyanines as the donor unit;[4] they are usually linked to C_{60} by long ether or ester bridges.[5] We report here on the total synthesis of a dyad that contains fullerene C_{60} bound to a chlorin by two methylene bridges and thus at a very small distance. The dyad, which is synthesized in an unusual one-pot reaction with concomitant formation of the chlorin macrocycle and linkage to the fullerene, is the first of this type that contains a chlorin moiety which is the chromophore in naturally occurring photosynthetic systems.

The starting point for the synthesis was the tripyrrolenickel complex *rac*-**3** (Scheme 1); we have already employed this complex in the synthesis of chlorins[6] and corrins.[7] After hydrolysis of the ester group in *rac*-**3**, the pyrrole aldehyde **2** was linked to tricyclic *rac*-**3** by decarboxylation and decomplexation. Subsequent recomplexation with zinc(II) or nickel(II) acetate gave the tetrapyrrolemetal complexes *rac*-**5a**, **b** and *rac*-**6a**, **b**. The robust nickel complex *rac*-**6a**, **b** was produced in order to characterize the tetracyclic compound. It was obtained as a separable binary mixture of diastereomers on account of the chiral center at C-1 and because of the helicity of the chromophore in the complex. The labile linear tetrapyrrolezinc complex *rac*-**5a**, **b** was cyclized upon heating in the presence of C_{60} to give the chlorin–fullerene dyad **7** along with the 15-cyano-substituted dyadic system **8** as a side product. This one-pot reaction is a complex cascade of single steps, the exact sequence of which has not yet been determined; however, it involves 1) loss of cyanide and formation of an enamine double bond at C-1, 2) cyclization between C-19 and the enaminoid double bond under the templating influence of the central zinc ion, 3) decarbobenzoxylation, 4) oxidation of the initially formed dihydrochlorin with atmospheric oxygen, 5) extrusion of sulfur dioxide, and finally 6) a Diels–Alder reaction between the diene formed and C_{60} as the dienophile to yield dyad **7**. The 15-cyano-

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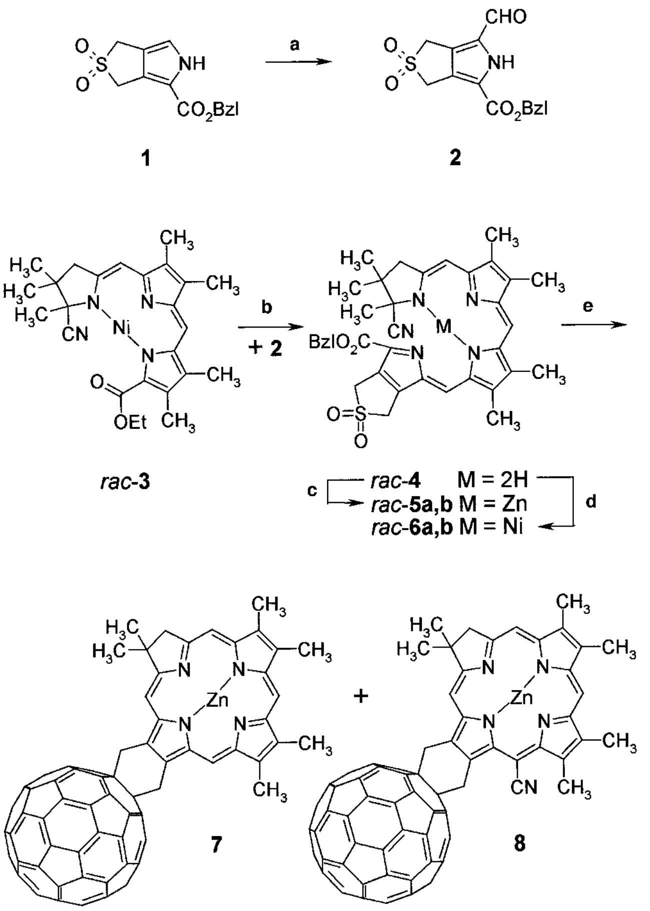


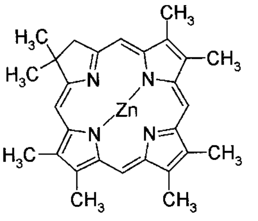
Scheme 1. Synthesis of the chlorin–fullerene dyad **7**. a) $POCl_3$, DMF, 90 °C, 1 h (73 %); b) 1.) 5 N KOH, MeOH/H_2O (9/1), THF, reflux, 45 min; 2.) **2** (1.8 equiv), *p*-TsOH, $CHCl_3$, reflux, 30 min; c) $Zn(OAc)_2$, NaOAc, room temperature, 20 min, chromatography, *rac*-**5a**, **b** (74 % based on *rac*-**3**); d) $Ni(OAc)_2 \cdot 4H_2O$, NaOAc, room temperature, 20 min, chromatography, *rac*-**6a** (39 % based on *rac*-**3**), *rac*-**6b** (37 % based on *rac*-**3**); e) *rac*-**5a**, **b**, C_{60} (2.6 equiv), 1,2,4-trichlorobenzene, 220 °C, 30 min, chromatography, **7** (32 %), **8** (4 %).

substituted side product **8** may be formed by the addition of cyanide to an intermediate dihydrochlorin.

Despite the complex course of reaction and the drastic reaction conditions, the total yield of 32 % is remarkably high. The average yield for the individual steps is 83 %. With regard to the synthesis of different chlorins, the cyclization method described here is considerably simpler than those previously reported.[6]

The corresponding ethyl ester of pyrrole **1**,[8] which serves as the starting material for the aldehyde building block **2**, cannot be formulated with a cannonical diene structure, in contrast to the macrotetracycle after the release of sulfur dioxide. Nevertheless it readily reacts with C_{60} to give the corresponding Diels–Alder adduct **10**.

The luminescence spectra (Figure 1) of the chlorin–fullerene dyad **7** and the bare chlorin **9** were compared after excitation at the wavelength of the Soret band (401 and 395 nm, respectively). The fullerene acceptor in **7** quenched the luminescence, whereas luminescence was observed for **9**. The quenching of the luminescence was independent of the concentration of dyad **7**, which indicates an intramolecular transfer of electrons or energy from the chlorin moiety to the fullerene moiety.



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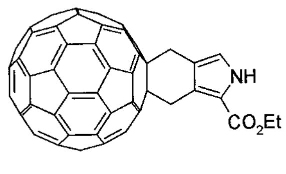

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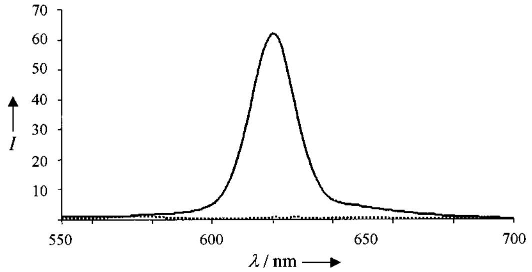

Figure 1. Fluorescence spectra of **7** (••••) and **9** (——) in $CHCl_3$ ($c = 10^{-6}$ M) after excitation at the individual Soret bands (401 and 395 nm, respectively).

Experimental Section

Selected spectroscopic data:

rac-**6a**: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.59, 0.79, 0.92$ (3s, 3 × 3H, 3 CH_3 at C-1 and C-2), 2.26 (d, $^5J = 0.77$ Hz, 3H), 2.28 (s, 6H), 2.40 (d, $^5J = 0.73$ Hz, 3H) (2.26–2.40: 4 CH_3 at C-7, C-8, C-12, and C-13), 2.53, 2.63 (AB system, $^2J_{AB} = 16.72$ Hz, 2H, 3-CH_2), 4.33, 4.49 (AB system, $^2J_{AB} = 15.77$ Hz, 2H, CH_2SO_2), 4.39, 4.48 (AB system, $^2J_{AB} = 14.88$ Hz, 2H, CH_2SO_2), 5.02, 5.27 (AB system, $^2J_{AB} = 12.37$ Hz, 2H, benzylester CH_2), 6.30, 6.70, 7.08 (3s, 3 × 1H, 5-H, 10-H, 15-H), 7.30 (m, 5H, Ph).

rac-**6b**: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.56, 1.09, 1.42$ (3s, 3 × 3H, 3 CH_3 at C-1 and C-2), 2.23 (d, $^5J = 0.85$ Hz, 3H), 2.26 (s, 6H), 2.35 (d, $^5J = 0.71$ Hz, 3H) (2.23–2.35: 4 CH_3 at C-7, C-8, C-12, and C-13), 2.35, 2.77 (AB system, $^2J_{AB} = 15.66$ Hz, 2H, 3-CH_2), 4.32, 4.46 (AB system, $^2J_{AB} = 15.71$ Hz, 2H, CH_2SO_2), 4.39, 4.48 (AB system, $^2J_{AB} = 14.84$ Hz, 2H, CH_2SO_2), 5.14, 5.26 (AB system, $^2J_{AB} = 12.44$ Hz, 2H, benzylester-CH_2), 6.18, 6.62, 6.99 (3s, 3 × 1H, 5-H, 10-H, 15-H), 7.26–7.30 (m, 5H, Ph).

7: *rac*-**5a**, **b** (5.0 mg, 7.0 µmol) and C_{60} (13.3 mg, 18.46 µmol, 2.63 equiv) were dissolved in 1,2,4-trichlorobenzene (5 mL). The mixture was boiled for 30 min with a bath temperature of 220 °C under argon and the solvent then removed in a bulb tube at 60 °C in a high vacuum. The residue was purified by chromatography on alumina (60 mL, neutral, activity II–III) with toluene to remove the unchanged C_{60} and then with dichloromethane/ethyl acetate (19/1). Isothermal recrystallization from dichloromethane/*n*-pentane gave **7**. Yield: 2.7 mg (2.24 µmol, 31.92 %). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.07$ (s, 6H, 2 CH_3 at C-2), 3.25, 3.35, 3.41 (3s, 12H, 4 CH_3 at C-7, C-8, C-12, and C-13), 4.57 (m, 2H, CH_2, C-3), 5.68, 5.74 (2s, 2 × 2H, 2 CH_2 at C-17 and C-18), 8.68, 8.83, 9.47, 9.82 (4s, 4 × 1H, H-5, H-10, H-15, H-20); UV/Vis ($CHCl_3$): $\lambda_{max}(\lg\varepsilon) = 705$ (extremely weak), 622 (4.29), 580 (3.90, plateau), 401 (4.69), 304 (4.44, sh), 257 (4.62); MS (MALDI-TOF, 9-nitroanthracene): m/z (%): 1204 (35) [M^+], 484 (100) [$M^+ - C_{60}$].

8: Selected spectroscopic data: UV/Vis ($CHCl_3$): $\lambda_{max}(\lg\varepsilon) = 658$ (4.20), 620 (3.42, plateau), 521 (3.29), 419 (4.45), 410 (4.41, sh), 311 (4.17, sh), 257 (4.52); MS (MALDI-TOF, 9-nitroanthracene): m/z (%): 1229 (22) [M^+], 509 (100) [$M^+ - C_{60}$].

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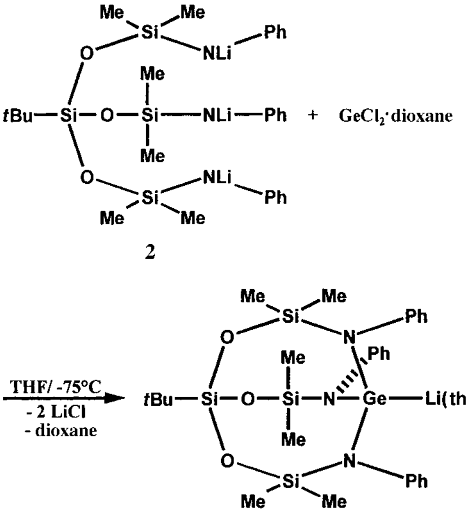
The First Crystal Structure of a Germanium(II) Amide with a Germanium–Lithium Bond and Its Behavior Towards Oxygen and Water**

Michael Veith,* Oliver Schütt, and Volker Huch

Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

Amides of Group 4 metals that contain metal–lithium bonds are relatively rare. A few years ago, Gade et al. reported the crystal structure of a tripodal silyl amide with a tin(II)–lithium bond.[1] A mixed germanium–lithium amide was also synthesized;[2] however, the structure of this compound could not be determined by X-ray structure analysis. In recent years only a few compounds containing germanium–lithium bonds have been synthesized and characterized by X-ray crystallography.[3–5] Very little is known about the chemistry of these compounds. We report here on the synthesis and crystal structure of a tripodal germanium(II) siloxamide with a germanium–lithium bond as well as on the reaction behavior of this bond towards water and oxygen. Interestingly, these reactions led to a simple Li/H exchange and an insertion of an oxygen atom into the germanium–lithium bond, respectively. We were able to isolate the reaction products from the hydrolysis and the oxidation and determine the structure of these compounds by X-ray crystallography.

The ligand system used was the tripodal amine *t*BuSi(OSi-$Me_2NHPh)_3$ (**1**);[6] its lithium salt **2**[6] was taken as the starting material for the synthesis of the germanium(II) siloxamide **3**. Compound **2** reacted with an adduct of germanium (II) chloride and dioxane[7] (equimolar amounts with respect to **2**) in THF at −75 °C to give the heterometallic amide **3** in good yields [Eq. (1)]. The ^1H, ^{13}C, ^{29}Si, and ^7Li NMR spectra of **3** in solution showed only one singlet each for the dimethylsilyl groups, for the methyl groups of the *tert*-butyl group, and for the lithium atom. This indicates that in solution **3** should have, at least on a time-average, C_{3v} symmetry. The ^1H and ^{13}C NMR spectra also contain signals for coordinated THF molecules.



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(1)

Controlled hydrolysis of **3** in THF gave the solvent-free germanium hydride **4** in 63 % yield [Eq. (2)] along with the soluble side product **1** (20–30 %). The remarkably simple Li/H exchange, for which there are only a few analogies,[8] can be explained by an attack of the oxygen atom of the water molecule on the Lewis acidic lithium atom of the Ge–Li bond. The proton transfers to the partially negatively charged germanium atom to yield **4** and lithium hydroxide. This corresponds to a change in the partial charge on the germanium atom since the proton is now regarded as a hydride. In the IR spectrum of the product the characteristic

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