[1] An extensive number of references are not listed here. For a recent general review, see: S. Borman, *Chem. Eng. News* **1998**, *76*, 47.
[2] A. H. Hoveyda, *Chem. Biol.* **1998**, *5*, R187.
[3] I. E. Maxwell, *Nature* **1998**, *394*, 325.
[4] R. F. Service, *Science* **1998**, *280*, 1670; B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648–2689; *Angew. Chem. Int. Ed.* **1999**, *38*, 2494–2532.
[5] Y. C. Yu, P. Berndt, M. Tirrell, G. B. Fields, *J. Am. Chem. Soc.* **1996**, *118*, 12515.
[6] T. Kunitake, *Pure Appl. Chem.* **1997**, *69*, 1999.
[7] K. Ariga, T. Kunitake, *Acc. Chem. Res.* **1998**, *31*, 371.
[8] G. B. Fields, R. L. Noble, *Int. J. Peptide Protein Res.* **1990**, *35*, 161.
[9] J. Nielsen, *Chem. Ind.* **1994**, 902.
[10] S. P. Spurlino, G.-Y. Lu, F. A. Quiocho, *J. Biol. Chem.* **1991**, *266*, 5202.
[11] J. A. Hall, K. Gehring, H. Nikaido, *J. Biol. Chem.* **1997**, *272*, 17605.

Selenium-Bridged Gold(I) Complex Cations $[Au_{10}Se_4(dppm)_4]^{2+}$ and $[Au_{18}Se_8(dppe)_6]^{2+}$**

Dieter Fenske,* Timo Langetepe, Manfred M. Kappes, Oliver Hampe, and Patrick Weis

The syntheses and possible applications of polynuclear complexes are presently being investigated by several research groups.[1] For instance, transition metal complexes have been reported in which the metal centers are bridged by main group element atoms.[2, 3] Sulfur-bridged cluster complexes of Groups 9 and 10 are among the known examples. Selenium- or tellurium-bridged compounds have been more rare up till now. However, chalcogen-bridged complexes of the coinage metals are predicted to feature physical properties of special interest. In contrast to the great number of known copper and silver compounds, only a few homologous gold species have been synthesized. This can certainly be attributed in part to the more restricted coordination chemistry of monovalent gold.[4, 5] The complexes are often stabilized by protecting phosphane ligands, which suppress further reaction to binary chalcogenides. According to quantum-chemical investigations of PR_3-substituted Cu_2E cluster complexes (R = organic group; E = S, Se), the compounds that have been characterized up to now appear to be metastable in most cases.[6] Nevertheless, the formation of various interesting molecules containing gold atoms has been described recently.[7] Examples are $[\{(Ph_3P)Au\}_4S]$ (Laguna et al.),[7h] $[\{CSAu(PPh_3)\}_6]$ (Schmidbaur et al.),[7i] and $[Au_{12}S_8]^{4-}$ (Strähle et al.).[7c] However, only a few reports concern chalcogen-bridged gold complexes which are clad by bidentate phosphane ligands.[8]

Herein $[Au_{10}Se_4(dppm)_4]Br_2$ (**1**) and $[Au_{18}Se_8(dppe)_6]X_2$ (**2**; X = Cl: **2a**, X = (PF_6): **2b**, X = BPh_4: **2c**; dppm = bis(diphenylphosphanyl)methane, dppe = bis(diphenylphosphanyl)ethane), two ionic compounds possessing such ligands and displaying remarkable stability, are introduced. Yellow crystals of **1** result from the reaction of $[(AuBr)_2(dppm)]$ with $Se(SiMe_3)_2$ [Eq. (1)].

$$5[(AuBr)_2(dppm)] + 4Se(SiMe_3)_2 \longrightarrow \underset{\mathbf{1}}{[Au_{10}Se_4(dppm)_4]Br_2} + 8Me_3SiBr + dppm \quad (1)$$

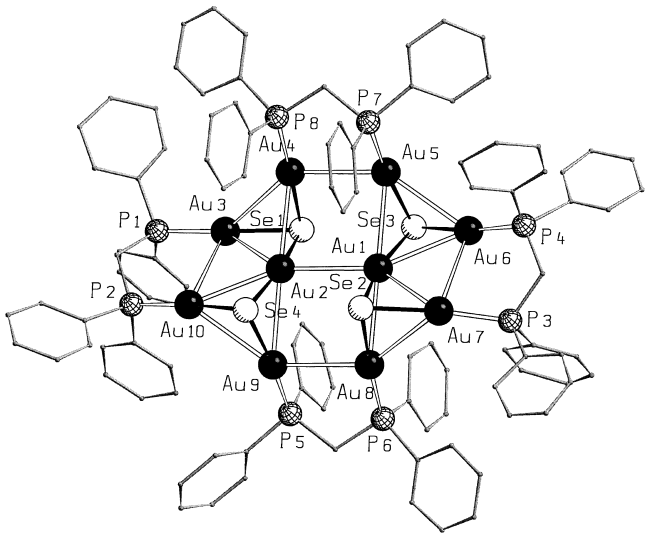

Figure 1. Structure of the cation of **1** in the crystal. Selected bond lengths [pm] and angles [°]: Au1–Au2 312.7(1), Au1–Au5 306.1(1), Au1–Se2 246.1(2), Au2–Au3 314.4(1), Au3–Au4 336.3(1), Au3–Au10, Au3–P1 227.8(6), Au3–Se1 242.9(2), Au4–Au5 309.6(1), Au4–Se1 242.3(2), Au4–P8 226.6(5), Se1–Se3 362.1(4); Au2-Se1-Au3 80.20(7), Au3-Au4-Au5 136.28(4), Au3-Au2-Au4 65.16(3), Au4-Au2-Au9 175.93(4), Se1-Au3-P1 168.5(2), Se1-Au4-P8 177.2(2), Se1-Au2-Se4 168.60(9).

The molecular structure of **1** was determined by single-crystal X-ray structure analysis.[9] In the cation of **1**, eight gold atoms (Au3–Au10) form an irregular, corrugated octagon which is centered by two further gold atoms (Au1, Au2; Figure 1). Thus, six Au_3 triangles and four Au_4 rectangles are generated. Four of the triangles (Au2, Au3, Au4; Au1, Au5, Au6; Au1, Au7, Au8; Au2, Au9, Au10) are μ_3-bridged by selenium atoms in such a way that the two neighboring Au_3 faces bind one selenium atom above and one below the average plane of the gold atoms. Selenium atoms which are positioned on the same side of the Au_{10} "plane" (Se1, Se3 and Se2, Se4) slightly approach each other through the Au_4 rectangle (Se1–Se3 362.1(4), Se2–Se 4372.4(4) pm). The peripheral gold atoms (Au3–Au10) additionally bind to one phosphorus atom of the dppm ligands. Each of these eight metal centers is therefore nearly linearly coordinated by one phosphorus and one selenium atom. In contrast, the inner gold atoms (Au1, Au2) bind almost linearly to two selenium

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neighbors. All Au–Se bond lengths (242.3(2) – 246.1(2) pm) lie within the expected range, and the angles at the gold centers (164.6(1) – 177.2(2)°) are somewhat smaller than the ideal angle of 180°. All Au-Se-Au angles in **1** are acute (76.3(1) – 87.8(1)°). Binding interactions between gold atoms can be excluded because of the long intermetallic distances (303.1(2) – 336.3(2) pm).

The reaction of $[(\mathrm{AuCl})_2(\mathrm{dppe})]$ with $\mathrm{Se(SiMe_3)_2}$ in dichloromethane gives orange crystals of **2a** in excellent yield [90 %, Eq. (2)]. Ensuing reactions of **2a** with $\mathrm{KPF_6}$ or $\mathrm{NaBPh_4}$ lead to the formation of **2b** and **2c**, respectively, ionic compounds consisting of a complex cation and sterically isolated anion molecules.

$$9[(\mathrm{AuCl})_2(\mathrm{dppe})] + 8\,\mathrm{Se(SiMe_3)_2} \longrightarrow \underset{\mathbf{2a}}{[\mathrm{Au_{18}Se_8(dppe)_6}]\mathrm{Cl_2}} + 16\,\mathrm{Me_3SiCl} + 3\,\mathrm{dppe} \qquad (2)$$

Single crystals of **2a** were characterized by X-ray diffractometry.[9] The molecular structure of the cation in **2a** is given in Figure 2. With regard to the heavy-atom substructure, a pseudo-threefold axis runs through selenium atoms Se1 and Se2. Two $[\mathrm{Au_9Se_4(dppe)_3}]$ fragments are interlocked in such a manner that a distorted $\mathrm{Au_6Se_2}$ heterocubane arrangement (Au1 – Au6, Se1, Se2) arises in the center of the polynuclear complex. This central $\mathrm{Au_6Se_2}$ unit is surrounded by the twelve remaining gold atoms that are attached to phosphorus atoms from dppe ligands. Within the $\mathrm{Au_6Se_2}$ heterocubane fragment, one finds Au–Au distances in the range between 294.0(2) and 300.2(2) pm; a range of 294.8(2) – 315.3(2) pm is observed for the outer gold atoms bonded to the heterocubane. Atoms Au7 – Au18 show intermetallic distances of 310.3(3) – 332.7(3) pm. Atoms Se1 and Se2 as well as the selenium atoms at the cation's periphery act as μ_3 bridges between gold atoms; the Au–Se bond lengths are 244.7(4) – 246.3(4) pm for Se1 and Se2. The peripheral selenium atoms each display three short Au–Se bonds (243.0(3) – 248.1(3) pm); there are also two weak interactions to neighboring gold atoms (332.4(4) – 373.3(4) pm). One perceives differences in the Au-Se-Au angle between selenium atoms that belong to the inner $\mathrm{Au_6Se_2}$ group those that are part of the outer Au–Se framework. For Se1 and Se2 these angles amount to 96.0(1) – 97.3(1)°, whereas the selenium atoms of the cluster periphery show Au-Se-Au angles in the wider range of 78.6(1) – 102.8(1)°. Similar observations have been reported for related compounds.[7b, 7f] If intermetallic contacts are not taken into consideration, each gold center is almost linearly coordinated by either two selenium neighbors (Au1 – Au6) or by one selenium and one phosphorus ligand (Au7 – Au18). Compound **2** features Se-Au-Se angles of 173.8(1) – 179.9(1)° at the inner gold atoms (Au1 – Au6); the remaining twelve gold centers (Au7 – Au18) form Se-Au-P angles in the range of 166.9(1) – 173.0(2)°. The Au–Se bond lengths (243.0(3) – 248.1(3) pm) are typical for such polynuclear complexes, and the Au–Au distances (294.0(2) – 332.7(3) pm) correspond with intramolecular Au–Au distances in $[\{\mu\text{-Au}_2(\mathrm{dppf})\}\{\mathrm{S}[\mathrm{Au_2(dppf)}]\}_2][\mathrm{OTf}]_2$ (290.5 – 327.2 pm; dppf = 1,1′-bis-(diphenylphosphanyl)ferrocene, OTf = trifluoromethanesulfonate (triflate)).[8b] The structural determinations of **2a – c** proved to be very problematic, since localization of the anion molecules was always frustrated by cocrystallization of disordered $\mathrm{CH_2Cl_2}$.

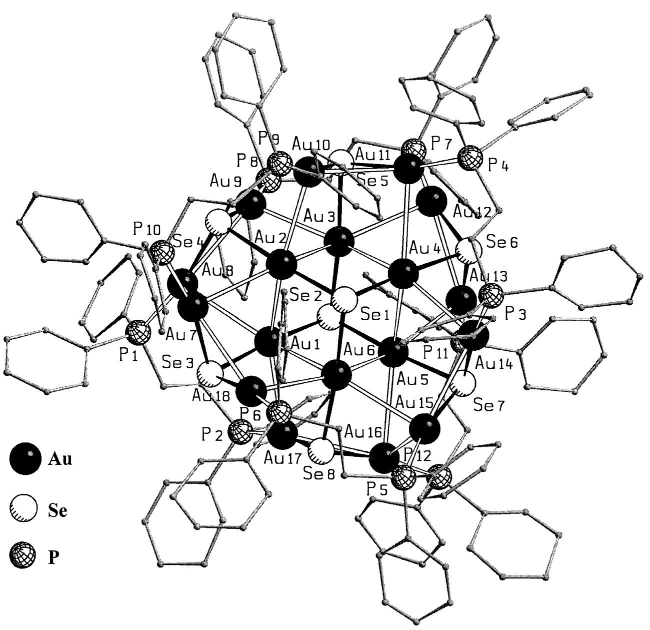

Figure 2. Structure of the cation of **2a** in the crystal. Selected bond lengths [pm] and angles [°]: Au1–Au2 294.3(2), Au1–Au8 312.4(2), Au1–Se2 246.3(4), Au1–Se3 247.8(4), Au7–Se3 245.4(4), Au7–P10 228.2(9); Au1-Se2-Au3 96.5(1), Au2-Au1-Au6 76.9(1), Au2-Au1-Se2 93.4(1), Au7-Se3-Au18 79.6(1), Se2-Au1-Se3 174.3(1), Se3-Au7-P10 166.9(2).

Nevertheless, the question concerning the charge of the cation and the nature of counterion could be answered unambiguously after electrospray/ionization mass spectrometry (ESI) experiments were carried out employing a high-resolution FT-ICR[12] mass spectrometer.

Figure 3 shows the cation mass spectrum of **2b**, which is dominated by one single peak. The high-resolution signal is shown along with the simulated isotopic distribution in the inset. Excellent congruence is observed for a distribution centered around m/z 3283.89, corresponding to the dication

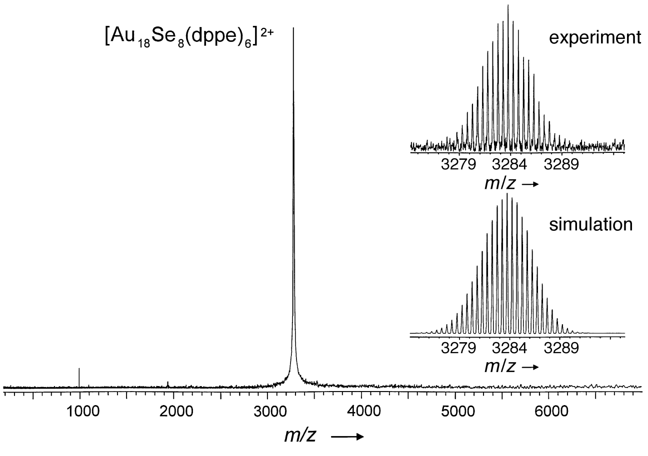

Figure 3. ESI mass spectrum of **2b** in $\mathrm{CH_2Cl_2}$ in the range of m/z 200 – 7000. Inset: Comparison of the experimentally observed high resolution molecular peak with the simulation.

$[Au_{18}Se_8(dppe)_6]^{2+}$. Thus the complex follows the classical perception of a gold(+I)/selenium(−II) compound. The actual charge distribution within the cluster and the possible existence of $d^{10}-d^{10}$ interactions, which were specified for binuclear gold complexes,[10] are the subject of further spectroscopic measurements as well as essential ab initio investigations.

The only anionic species found in the mass spectrum of **2b** is PF_6^-. This clearly shows that a complete metathesis reaction took place followed by integration of the new anion molecules in the lattice.

It was thus possible to vaporize an inorganic ionic compound featuring a molecular mass of about 6568 g mol^{-1} almost without fragmentation by means of electrospray experiments.

A second mass spectrometric measurement was performed to investigate collision-induced fragmentation of the dication in **2b** by argon. The preferred dissociation path was found to be a scission of the complex framework into the fragments $[Au_5Se_2(dppe)_2]^+$ and $[Au_{13}Se_6(dppe)_3]^+$ with loss of one phosphane molecule. This directly suggests that the Au−Se and the Au–phosphane binding energies are of the same order of magnitude. More intensive studies of the dissociation behavior of the presented polynuclear complex is the subject of another publication.[13]

The experimental observations indicate a high stability of the cationic molecular framework fo **2**. Furthermore, it is conspicuous that **2** dissolves only in particular solvents, such as CH_2Cl_2, DMF, or pyridine. The complex is stable to air and moisture and does not decompose below 80 °C.

Reactions of $[(AuCl)_2(dppe)]$ with Me_3SiSeR (R = Et, *i*Pr, *t*Bu, *n*Bu) always yield **2a**, indicating that Se−C bond cleavage invariably occurs. The cation in **2** is so energetically advantaged, that it has not been possible yet to produce or isolate complexes containing SeR^- ligands by the described route.

Besides **2**, isostructural Au−Te species could be synthesized that are ligated by dppe, dppa, or dppb ligands (dppa = bis(diphenylphosphanyl)ethyne, dppb = bis(diphenylphosphanyl)butane).

In conclusion, reactions of gold halide–phosphane complexes with silylated selenium derivates yield very stable polynuclear gold complexes. By means of single-crystal X-ray structure analyses, the following compounds were structurally determined: $[Au_{10}Se_4(dppm)_4]Br_2$, $[Au_{18}Se_8(dppe)_6]Cl_2$, $[Au_{18}Se_8(dppe)_6][BPh_4]_2$, $[Au_{18}Se_8(dppe)_6][PF_6]_2$. Electrospray mass spectrometry experiments of $[Au_{18}Se_8(dppe)_6][PF_6]_2$ (**2b**) show an enormous stability of the complex. Collision-induced fragmentation by argon provokes splitting into three fragments.

Experimental Section

1: $[(AuBr)_2(dppm)]$ (1 mmol, 940 mg) was suspended in CH_2Cl_2 (10 mL) and then $Se(SiMe_3)_2$ (1 mmol, 0.25 mL) was added at room temperature. The slight yellow solution was stirred for 2 h and layered with *n*-heptane (10 mL). Pale yellow crystals of **1** were obtained in 67 % yield.

2: $[(AuCl)_2(dppe)]$ (1 mmol, 860 mg) was suspended in CH_2Cl_2 (10 mL) and then $Se(SiMe_3)_2$ (0.88 mmol, 0.22 mL) was added at room temperature. Within 5 min the solution turned orange. After 4 h of stirring the solution was layered with *n*-heptane (10 mL). Orange needlelike crystals grew within 1 d, during which the solution discolored. Compound **2a** was produced in 90 % yield. Subsequently, the solution was removed by pipette and the crystals were redissolved in CH_2Cl_2 (10 mL). KPF_6 or $NaBPh_4$ (2 mmol) wsa then added, and the reaction mixture stirred for 2 h. Removal of the solid material and layering with *n*-heptane (10 mL) led to the formation of orange crystals of **2b** or **2c**, respectively, in 75 % yield.

The Au, Se, P, and C elemental analyses of **1** and **2a**–**c** corresponded to the given formulas.

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[1] *Clusters and Colloids. From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**.

[2] See, for example, a) L. C. Roof, J. W. Kolis, *Chem. Rev.* **1993**, *93*, 1037; b) I. Dance, K. Fisher, *Prog. Inorg. Chem.* **1994**, *41*, 637; c) J. Arnold, *Prog. Inorg. Chem.* **1995**, *43*, 353.

[3] a) D. Fenske, J. Ohmer, J. Hachgenei, *Angew. Chem.* **1985**, *97*, 933; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 993; b) D. Fenske, J. Ohmer, J. Hachgenei, K. Merzweiler, *Angew. Chem.* **1988**, *100*, 1300; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1277.

[4] a) H. W. Roesky, T. Gries, P. G. Jones, K.-L. Weber, G. M. Sheldrick, *J. Chem. Soc. Dalton Trans.* **1984**, 1781; b) S.-P. Huang, M. G. Kanatzidis, *Inorg. Chem.* **1991**, *30*, 1455; c) V. W. W. Yam, W. K. Lee, T. F. Lai, *J. Chem. Soc. Chem. Commun.* **1993**, 1571; d) P. J. Bonasia, G. P. Mitchell, F. J. Hollander, J. Arnold, *Inorg. Chem.* **1994**, *33*, 1797; e) V. W. W. Yam, K. K. W. Lo, C. R. Wang, K. K. Cheung, *Inorg. Chem.* **1996**, *35*, 5116; f) V. W. W. Yam, K. K. W. Lo, *Comments Inorg. Chem.* **1997**, *19*, 209.

[5] a) D. Fenske, H. Krautscheid, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, *105*, 1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1303; b) S. Dehnen, D. Fenske, A. C. Deveson, *J. Cluster Sci.* **1996**, *7*, 351; c) S. Dehnen, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 1407; d) A. C. Deveson, S. Dehnen, D. Fenske, *J. Chem. Soc. Dalton Trans.* **1997**, 4491; e) J. F. Corrigan, D. Fenske, *Chem. Commun.* **1997**, 1837; f) D. Fenske, N. Zhu, T. Langetepe, *Angew. Chem.* **1998**, *110*, 2783; *Angew. Chem. Int. Ed.* **1998**, *37*, 2639.

[6] a) S. Dehnen, A. Schäfer, D. Fenske, R. Ahlrichs, *Angew. Chem.* **1994**, *106*, 786; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 746; b) A. Schäfer, R. Ahlrichs, *J. Am. Chem. Soc.* **1994**, *116*, 10686; c) S. Dehnen, A. Schäfer, R. Ahlrichs, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 429.

[7] a) P. G. Jones, G. M. Sheldrick, E. Hädicke, *Acta Crystallogr. Sect. B* **1980**, *36*, 2777; b) C. Lensch, P. G. Jones, G. M. Sheldrick, *Z. Naturforsch. B* **1982**, *37*, 944; c) G. Marbach, J. Strähle, *Angew. Chem.* **1984**, *96*, 695; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 715; d) P. G. Jones, C. Thöne, *Chem. Ber.* **1990**, *123*, 1975; e) I. Schröter, J. Strähle, *Chem. Ber.* **1991**, *123*, 2161; f) S. P. Huang, M. G. Kanatzidis, *Angew. Chem.* **1992**, *104*, 799; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 787; g) H. Schmidbaur, A. Kolb, E. Zeller, A. Schier, H. Beruda, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1575; h) F. Canales, M. C. Gimeno, P. G. Jones, A. Laguna, *Angew. Chem.* **1994**, *106*, 811; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 769; i) H. K. Yip, A. Schier, J. Riede, H. Schmidbaur, *J. Chem. Soc. Dalton Trans.* **1994**, 2333.

[8] a) S. Hofreiter, M. Paul, H. Schmidbaur, *Chem. Ber.* **1995**, *128*, 901; b) F. Canales, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Am. Chem. Soc.* **1996**, *118*, 4839; c) V. W. W. Yam, E. C. C. Cheng, K. K. Cheung, *Angew. Chem.* **1999**, *111*, 193; *Angew. Chem. Int. Ed.* **1999**, *38*, 197.

[9] X-ray structure analyses: STOE-IPDS ($Mo_{K\alpha}$ radiation); data collection and refinement(SHELXS-86, SHELXL-93); empirical absorption correction (habit). **1**: monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, cell parameters(190 K): $a = 1086.0(2)$, $b = 4054.0(8)$, $c = 2916.0(6)$ pm, $\beta = 92.58(3)^\circ$, $V = 12825.5(5) \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 13.498$ mm^{-1}, $2\Theta_{max} = 46{,}38^\circ$; of 19923 reflections, 12783 were independent, 12759 with $I > 2\sigma(I)$, 1233 parameters (Au, Se, P anisotropic, C isotropic); max. residual electron density 3.3 e Å^{-3}; $R_1 = 0.05$; $wR_2 = 0.15$. **2a**: monoclinic, space group $P2_1/n$ (Nr. 14), $Z = 4$, cell parameters (200 K): $a = 1779.1(4)$, $b = 3987.7(8)$, $c = 2934.8(6)$ pm, $\beta = 92.37(3)^\circ$, $V = 20803 \times 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 14.433$ mm^{-1}, $2\Theta_{max} = 46{,}52^\circ$; of 28286 reflections, 28282 were independent, 22915 reflections with $I > 2\sigma(I)$, 1077 parameters (Au, Se, P anisotropic, C isotropic); max. residual electron density 8.5 e Å^{-3}; $R_1 = 0.10$; $wR_2 = 0.27$. The high R values were caused by highly disordered solvent molecules that could not be localized; localization of the anions was

not possible either. 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-140363 (**1**) and CCDC-140364 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] W.-F. Fu, K.-C. Chan, V. M. Miskowski, C.-M. Che, *Angew. Chem.* **1999**, *111*, 2953; *Angew. Chem. Int. Ed.* **1999**, *38*, 2783.

[11] a) J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science* **1989**, *246*, 46; b) *Electrospray Ionization Mass Spectrometry* (Ed.: R. B. Cole), Wiley, New York, **1997**, and references therein.

[12] *F*ourier *t*ransform-*i*on *c*yclotron *r*esonance (FT-ICR) mass spectrometry: A. G. Marshall, P. B. Großhans, *Anal. Chem.* **1991**, *63*, 215A.

[13] P. Weis, O. Hampe, M. M. Kappes, T. Langetepe, D. Fenske, unpublished results.

Channel-Forming Peptaibols Are Potent Elicitors of Plant Secondary Metabolism and Tendril Coiling**

Jürgen Engelberth, Thomas Koch, Frank Kühnemann, and Wilhelm Boland*

Attack by microorganisms and herbivorous insects may induce characteristic local and systemic responses in plants. Typical defense reactions include de novo biosynthesis of phytoalexins and, characteristic of insect damage, the emission of volatile compounds for long-distance interactions.[1, 2] The molecular basis for recognition of either infection or herbivore interference at the plant's cell surface, however, is not well understood. The signal chain is often triggered by compounds from the attacking organism, generally referred to as elicitors. Subsequent intracellular signal transduction involves changes in the ion permeability of the plasma membrane,[3] which initiates a complex network of intracellular events leading to an increase of biosynthetic activities. The involvement of ion channels in signaling was previously demonstrated with parsley cells and an oligopetide elicitor,[4] with tobacco cells and oligogalacturonides,[5] and, more recently, with several proteinaceous elicitors involved in phytoalexin biosynthesis in plants.[6]

In addition to macromolecular elicitors, certain fungi also produce low molecular weight peptide-type antibiotics with membrane-depolarising properties.[7] Characteristic features of their chemical structures are the acylated N terminus, and the presence of α-aminoisobutyric acid (Aib) and C terminal α-amino alcohols (peptaibols). They occur mainly as large 18- to 20-membered peptaibols, such as alamethicin,[7] ampullosporin[8] and chrysospermin,[9] and as smaller 15- to 16-membered species, such as antiamoebin.[10] Their antimicrobial activity is largely due to the formation of α-helical structures which produce voltage-dependent or voltage-independent ion channels within biological membranes.[7, 11] Since the induction of phytoalexin biosynthesis in plants may be directly linked to ion fluxes and subsequent intracellular signaling,[3, 4] this property of the peptaibols prompted us to study their potential effect on the secondary metabolism of plants.

Here we demonstrate for the first time that fungal peptaibols represent a novel and powerful class of elicitors that can induce multiple metabolic activities such as ethylene emission, biosynthesis of volatile substances, and tendril coiling.

As a representative model compound we chose alamethicin (ALA), a mixture of homologous peptaibols from the wide spread soil fungus *Trichoderma viride*, the major component of which contains eight Aib residues and two prolines.[7, 11] The N terminus is acetylated, and the C-terminal residue is phenylalaninol (Table 1). ALA is capable of forming voltage-gated channels which exhibit very high conductance in lipid membranes.[7, 11]

When ALA (5 μM) was supplied to the shoots of young Lima bean plants (*Phaseolus lunatus*) through the transpiration stream,[12] subsequent monitoring of the surrounding gas phase in a continuous flow system by photoacoustic spectroscopy[13, 14] revealed the emission of ethylene as one of the plant's earliest responses to the peptaibol (Figure 1a). The emission of ethylene started approximately 3 h after the onset of the stimulus, reached a transient maximum after about 7.5 h and leveled off during the following 5 h; this response resembles the profile of ethylene emission after induction with the proteinaceous elicitor cellulysin[14] or with jasmonic acid.[15] Continued monitoring of the gas phase by absorption of emitted volatile compounds onto activated carbon in a closed system,[12] followed by desorption and mass spectrometric analysis of the trapped compounds, demonstrated that the biosynthesis of certain terpenoids and aromatic components had also been increased by the treatment with ALA. The gas chromatogram (Figure 1b) shows that DMNT (5%) and methyl salicylate (MeSA) (4%) are the main compounds formed after TMTT (91%). Interestingly, the same profile of terpenoids can be induced by treatment of Lima bean leaves with 12-oxophytodienoic acid (12-OPDA),[12] an early biosynthetic precursor of jasmonic acid (JA). JA itself, provokes a more complex pattern of volatile compounds when applied to Lima bean leaves.[15] The induction of volatile compound biosynthesis by ALA was dose dependent with a threshold concentration in the range of approximately 0.5 μM.

Owing to the presence of MeSA in the gas phase and the induction of biosynthesis of terpenoids, which represent a

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