of **3**, a dose of 5 μmol kg^{-1} induced 60% regression.[18] These results suggest that the introduction of bulky perfluoroalkyl groups results in higher tumor regression at lower photosensitizer doses; the molecular and pharmacological reasons for the differences between **2** and **3** in vivo remain to be elucidated.

In summary, our results provide a simple (classical) yet efficient approach to nonplanar perhalogenated phthalocyanines, of which [F_{64}PcZn] is only the first representative. Other metals and R^F groups will yield compounds with a diversity of size, shape, and depth of fluorinated cavities around a reactive metal center. Their thermal, photochemical, and chemical stability, coupled with their potential synthetic versatility and favorable solubility, suggest that this class of molecules might be effective for photophysical, chemical, and perhaps, medical uses. Applications requiring stability under harsh conditions and/or aggressive reagents, or solubility in nonconventional solvents might be considered.

Experimental Section

2: A mixture of zinc acetate (0.123 g, 0.668 mmol) and **1**, (1.337 g, 2.67 mmol) was heated under Ar at 180 °C for 60 min. Chromatography on silica gel using 20–30% acetone/hexanes, followed by diffusion of hexanes into an acetone solution gave crystalline **2** in 21% yield; m.p. > 300 °C; FAB MS [*m/z*] 2064.84 [M^+]. Elemental analysis: calcd (%) for $ZnC_{63.5}H_{15}N_8O_{2.5}F_{64}$: ($ZnC_{56}N_8F_{64} \cdot 2.5$ acetone), C 34.49, H 0.68, N 5.07; found: C 34.38, H 0.73, N 5.09. The extra half acetone molecule was not detected crystallographically. ^{19}F NMR (376.497 mHz, [D$_6$]acetone, $CFCl_3$): $\delta = -71.3$ (6F), -103.9(1F), -164.6 (1F); ^{13}C NMR (100.613 mHz, [D$_6$]acetone): $\delta = 154.6$, 152.0, 130.9, 121.5, 117.5, 95.2. UV/Vis [nm] (log ε), acetone, 322 (4.38), 396 (4.56), 620 (4.42), 686 (5.24).

Biological tests: Suspensions of **2** or **3** in 10% CRM (CRM = cremofor) were administered intravenously. The tumors were illuminated with 650–700 nm light (1 kW Xenon lamp, LL650 and LS700 filters) at fluence rates of 200 mW cm^{-2}, 400 J cm^{-2} per tumor. Absence of a palpable tumor three weeks post irradiation was considered regression.

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Synthesis and Structure of a Biconcave Cobalt Perfluorophthalocyanine and Its Catalysis of Novel Oxidative Carbon–Phosphorus Bonds Formation by Using Air[**]

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One of the major challenges of modern chemistry, homogeneous aerobic oxidations, poses the additional challenge of designing suitable catalysts that are not only active, but resist self-oxidation as well. For transition metal complexes, this

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means shifting the chemistry from ligand oxidation (internal substrate) to oxidation of an external substrate. In addition, the replacement of byproduct-generating or stoichiometric oxidation reactions with catalytic ones is preferable, and environmentally benign.

We have recently reported that replacing all the C–H groups adjacent to the copper site of a hemocyanine model by C–F groups leads to reversible O_2 binding at ambient conditions without ligand decomposition.[1a, b] We extend this strategy from non-heme to heme-type complexes and report the first peripherally substituted perfluorinated cobalt phthalocyanine. In both this and a related zinc analogue, (preceding paper)[1c] the bulky substituents induce a nonplanar, biconcave character relative to the planar, unsubstituted perhalogenated metallophthalocyanines. We also report that the cobalt complex catalyzes the oxidative formation of carbon–phosphorus double bonds. Porphyrin[2] and phthalocyanine (Pc) based[2a, 3] complexes are known to catalyze the oxidation of various organic substrates, but they do not catalyze this reaction, which to the best of our knowledge is not known to occur oxidatively.

The cobalt complex, $[F_{64}PcCo(acetone)_2]$ (**1**), was prepared by treating perfluoro-(4,5-di-isopropyl)phthalonitrile[4] with cobalt acetate and crystallizing the product from acetone. This strategy yields a single isomer, unlike the direct free-radical substitution of fluorine in cobalt perfluorophthalocyanine $[F_{16}PcCo]$ by linear alkyl groups, which yields an ill-defined mixture of isomers of unknown structures and composition.[5]

The steric interactions of the *ortho* iC_3F_7 groups observed in the dinitrile precursor[4] and the zinc structures are maintained;[1c] the minimum energy conformation of the two methine fluorine atoms results in orientation of the CF_3 groups above and below the aromatic ring (Figure 1 b), which creates a pocket in which acetone resides (Figure 1 c). The cobalt complex **1** is deep blue and, in comparison with the parent cobalt phthalocyanine $[H_{16}PcCo]$, or cobalt perfluorophthalocyanine $[F_{16}PcCo]$, significantly more soluble in organic solvents. Large single crystals of **1** form readily,[6] in contrast to strictly planar halogenated phthalocyanines. The phthalocyanine ring is planar, with the cobalt atom at its geometric center. The Co–O bond (2.314 Å) is longer than the average Co^{II}–O(acetone) bond (2.196 Å; range 2.177–2.289 Å) of the three reported cobalt(II)–acetone complexes.[7–11] Despite the long Co–O bonds, **1** does not lose solvent in the solid state at ambient conditions. The other bond lengths and angles appear normal, but a comparison with other fluorine-substituted phthalocyanine structures cannot be performed since none are reported.[7] The van der Waals surface of **1**, Figure 1 c, defines the "Teflon-coated" fluorine-lined cavity around the metal center. In comparison with aromatic C–F groups, the exclusively aliphatic C–F groups (present also on the surface of Teflon coatings), adjacent to the cobalt, are less susceptible to nucleophilic attack and confer enhanced chemical and thermal robustness to the immediate metal environment. Two symmetry-related acetone molecules reside in the fluorine-lined cavities. Because of the sp^2 hybridization of the coordinated carbonyl oxygen atom, only one CH_3 group of each acetone protrudes outside and is thus exposed to the environment. In contrast to the zinc structure,[1c] the acetone in the cobalt complex appears more ordered.

Addition of excess triphenylphosphane under ambient conditions to a solution of **1** in acetone triggers an immediate color change from blue to purple. The characteristic 668 nm Q-band absorption of **1** shifts 42 nm to 710 nm. Evaporation of the acetone solution gives purple X-ray quality crystals of the $[F_{64}PcCo(1\text{-triphenylphosphoranylidene-2-propanone})_2]$ (**2**; Figure 2).[12]

The structure reveals that triphenylphosphane has coupled with both coordinated acetone molecules of **1** to form two molecules of the keto-stabilized ylide [Eq. (1)], 1-triphenylphosphoranylidene-2-propanone (henceforth called ylide), part of the complex $[F_{64}PcCo(ylide)_2]$ (**2**).

$$Ph_3P + R{-}CH_3 + \tfrac{1}{2}O_2 \longrightarrow Ph_3P{=}CH{-}R + H_2O, \text{ where R is } C({=}O)CH_3 \quad (1)$$

This reaction does not occur in the absence of air. Both *trans* acetone molecules couple, in overall quantitative yield, based upon cobalt. In general, coordinated acetone is labile, even if the metal is complexed by sterically demanding ligands. In particular, the reaction of Ph_3P with such complexes results in acetone substitution. For example, Kläui's O_3-tripodal ligand, $[(\eta^5\text{-}C_5H_5)Co\{P({=}O)(OMe)\}_3]$ (L), forms half-sandwich [LM(anion)(acetone)] complexes, $M = Co^{II}$ and Ni^{II}.[10, 11] The acetone of the nickel complex, isostructural with the cobalt complex, is easily substituted by Ph_3P. In

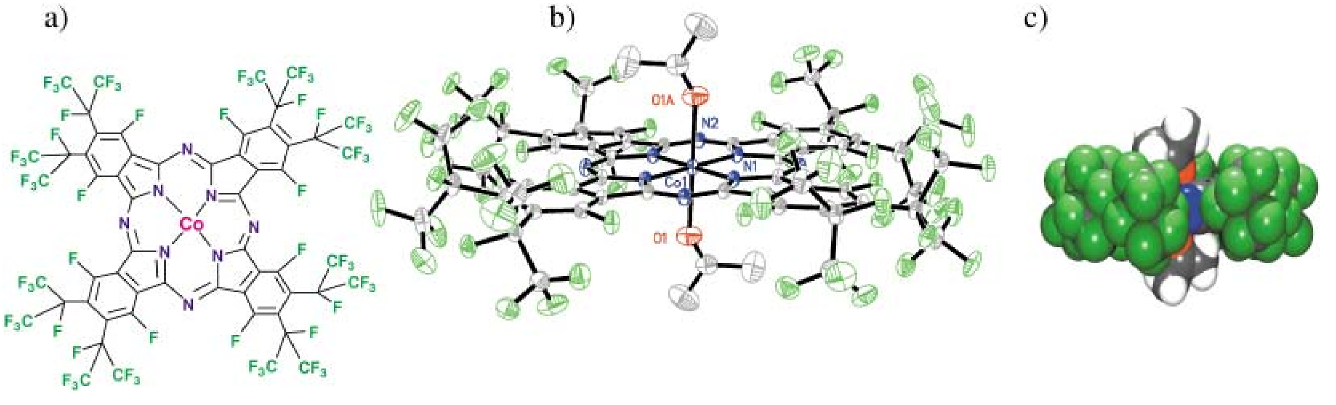

Figure 1. **1**: a) structural formula (acetone molecules omitted); b) X-ray structure with thermal ellipsoids set at 30 % probability (H atoms of the acetone molecules are omitted); c) space-filling representation viewed along the phthalocyanine ring; F green, N blue, O red, C gray, H white.

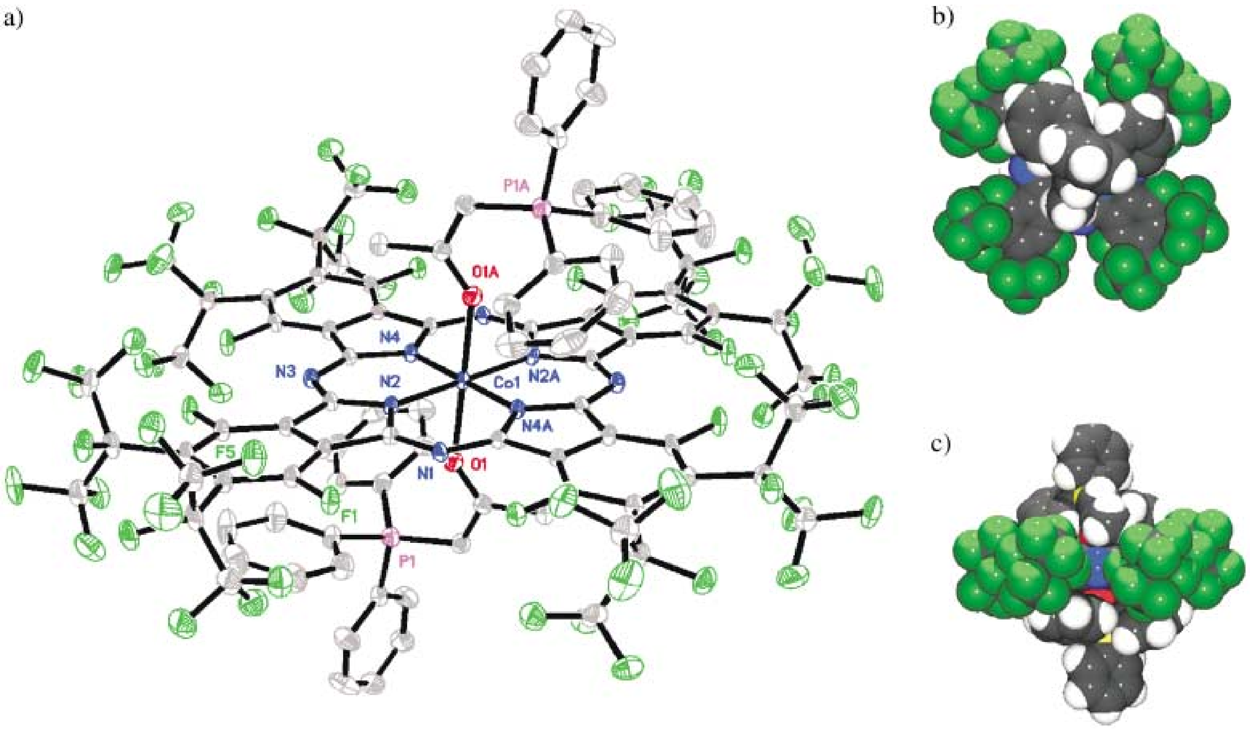

Figure 2. **2**: a) X-ray structure with thermal ellipsoids set at 30 % probability (H atoms omitted); b) space-filling representation viewed perpendicular to the phthalocyanine ring; c) space-filling representation viewed along the phthalocyanine ring; F green, N blue, O red, C gray, P purple.

contrast, the acetone molecules of **1** react with Ph$_3$P, rather than being replaced by it.

The geometry of the F$_{64}$PcCo moiety of **2** is similar to that of its [F$_{64}$PcCo(acetone)$_2$] precursor. The 1.259(5) Å C=O and 1.723(4) Å methine carbon–phosphorous bonds in **2** are slightly below the 1.275–1.333 Å (average 1.292 Å) and 1.732–1.773 Å (average 1.752 Å) values observed for the other three, Ti,[13] Sn,[14] and Pd,[15] structurally characterized metal–ylide compounds; in contrast, the methine carbon–carbonyl carbon bonds are longer, 1.383(5) Å versus 1.333–1.366 Å (average 1.353 Å). Taken collectively, the structural differences suggest only a small negative charge (if any) on the coordinated carbonyl oxygen atom. On the other hand, the infrared spectrum of **2** shows a ν_{co} band at 1509 cm^{-1}, a value which is 34 cm^{-1} lower than the correponding ν_{co} band of the free 1-triphenylphosphoranylidene-2-propanone (1540 cm^{-1})[16]. This shift suggests the presence of a significant negative charge on the coordinated carbonyl oxygen atom. Despite the low ν_{co} value the ylide unit in **2** appears to be geometrically closer to the free ylide (the X-ray structure of which has not been reported), as is consistent with the relatively long Co–O bonds (2.221(3) Å).

We ascribe the relative stability of the ylide complex (which allowed its isolation) to the electron-withdrawing effect of the fluorine groups, which enhances the Lewis acidity of the metal center, combined with the effect of the tight fit of the ylide inside the F$_{64}$PcCo pocket. One of the phenyl rings of the ylide group, which is almost parallel to the Pc ring (16° dihedral angle, Figure 2b) and only 3.8 Å away from it may provide additional stabilization by π–π stacking interactions. Because of the ylide penetration inside the F$_{64}$PcCo cavity, a second phenyl ring also tends to become parallel with the Pc ring (Figure 2b, c). As a result, its contact with the first ring, as measured by the *meta* C(phenyl)–C(phenyl) inter-ring distance, is 3.455 Å, a value lower than that of 84.7 % of the over 2100 *meta–meta* contacts reported[7] for Ph$_3$P. The tight fit (steric repulsions), however, may prevent the carbonyl oxygen atom from freely approaching the metal center and thus hampers the formation of a stronger cobalt–oxygen bond. For the same steric reason the Ph$_3$P group may not be able to penetrate sufficiently deep inside the cavity to coordinate to the metal center. A contributing factor may be the mismatch between the three-fold symmetry of Ph$_3$P and four-fold symmetry of the cavity, which prevents the alignment of the Ph$_3$P phenyl rings along the cavity grooves (see Figure 2b, c).

Notably, there are no first-row transition metal ylide complexes structurally characterized; the reaction of ylide with CoCl$_2$ does not result in coordination.[17]

The similar geometry and position of the ylide (product) and acetone (reactant), on the one hand, suggests that 1) the coupling with Ph$_3$P does not require a significant reorganizational activation energy of the precursor and 2) only the exposed methyl group is available for coupling despite the large excess of Ph$_3$P. The similarity in the geometry of the coordinated and free ylide, on the other hand, suggests that the coordinated ylide might be labile in solution. Complexes **1** and **2** are in equilibrium in acetone; addition of excess coordinating solvent to **2** results in the liberation of the ylide and regeneration of **1**. Column chromatography allows the facile separation of the ylide. After removing the excess acetone by rotoevaporation the equilibrium is shifted back towards **2** and the process can be repeated as long as there is free Ph$_3$P. This catalytic cycle, which can be monitored by UV/Vis spectroscopy, has been performed numerous times, each time producing the ylide complex **2** in quantitative yield (based upon the cobalt complex). No decomposition of the catalyst was observed.

Both the appropriate metal and the steric bulkiness of the ligand appear essential for catalysis. Thus, neither the sterically analogous $[F_{64}PcZn(acetone)_2]$,[1c] nor the unhindered, *two-dimensional* cobalt perfluorophthalocyanine complexes $[F_{16}PcCo]$ and $[H_{16}PcCo]$ form 1-triphenyl-phosphoranylidene-2-propanone with Ph_3P even after several days under reflux in acetone. Saturated acetone solutions of either $[F_{16}PcCo]$ or $[H_{16}PcCo]$ do not even complex 1-triphenylphosphoranylidene-2-propanone.

The aromatic 1-triphenylphosphoranylidene-2-propanone is relatively stable and a valuable chemical reagent. Aliphatic, electron-rich, 1-trialkylphosphoranylidene-2-propanones, on the other hand, are not used extensively.[18] Indeed, only the methyl, ethyl, and butyl derivatives are reported.[19] Their preparation can be accomplished by the stoichiometric acetylation of phosphorus ylides, $R_3P{=}CH_2$, with an acetyl metal complex, or acetyl chloride. The latter reagent, however, yields the diacetyl derivative as well. The products are unstable and decompose with the production of phosphane oxides.[19] The lack of applications and stability notwithstanding, we have explored the oxidative formation of 1-tributylphosphoranylidene-2-propanones by treating acetone with the corresponding phosphane, Bu_3P. The same blue to purple color change, as observed in the reaction with Ph_3P, occurs in the visible region. The UV/Vis spectra of the product derived from Bu_3P is virtually identical to that of the product from the reaction with Ph_3P, which suggests that the corresponding complex, $[F_{64}PcCo(1\text{-tributylphosphoranylidene-2-propanone})_2]$ (**3**) forms in solution. Isolation of **3** or the phosphorane under ambient conditions, however, leads to partial decomposition, but both can be detected by mass spectrometry. Optimization of this reaction was not pursued because of its limited utility.

The combination of the nonplanar biconcave nature of the phthalocyanine, the type of metal (redox or non-redox) and the strong electron-withdrawing effects of the fluorine groups, appears to be critical for reactivity. In addition, the fluorinated pockets of the phthalocyanine complexes appear to both stabilize and promote the coupling reaction of the coordinated acetone molecules.

Noteworthy is that ylides, useful Wittig reagents, are generally prepared by a different route.[20–22] Starting with a molecule with C–H groups, RCH_3, a halogenated derivative, RCH_2X, is formed by the reaction with a halogen. Next, the carbon–phosphorous bonds are formed [Eqs. (2), (3)].

$$RCH_2X + Ph_3P \longrightarrow Ph_3P^{+}{-}CH_2RX^{-};\ X = Cl, Br \qquad (2)$$

$$Ph_3P^{+}{-}CH_2RX^{-} + B^{-}M^{+} \longrightarrow Ph_3P{=}CHR + BH + MX;\quad B = \text{base},\ M = \text{metal} \qquad (3)$$

$B^{-}M^{+}$ is a metal hydroxide (in aqueous environments) or *n*-butyl lithium (in non-aqueous environments). To form the ylide, two hydrogen atoms of a substrate are removed by halogen atoms, which do not became part of the product. Our observations indicate that these hydrogen atoms could be removed catalytically as water, with no need for halogen atoms, by using air at ambient conditions [Equation 1]. This type of carbon–phosphorus coupling extends the classical synthesis of Wittig reagents.

In summary, we report the facile preparation of the first representative of a novel class of robust homogeneous catalysts. This material resembles an enzyme because of the presence of a heme-like metal center buried inside a sterically restricting, but robust cavity that, as shown above, is essential for catalysis. The enzyme-like complex can couple phosphanes with acetone to produce ylides and water at ambient conditions, by using air (as opposed to halogenated chemicals) as the sole reagent. This chemistry might afford the replacement of the classical stoichiometric keto–ylide formation reaction by a catalytic process.

Work aimed at elucidating the mechanistic details and extending both this catalyst class and the scope of the oxidation chemistry to other substrates is in progress.

Experimental Section

1: A mixture of perfluoro-(4,5-di-isopropyl)phthalonitrile,[4] (2.253 g, 4.505 mmol) and cobalt(II) acetate, (0.199 g, 1.123 mmol) was heated under argon to 230 °C for 100 min. The color changed to deep green. After cooling, the mixture was purified by chromatography on silica gel using 10% acetone/pentane to give **1** in 34.5% yield. M.p. > 300 °C; MS (FAB, NBA): 2057 $[M^{+}]$; UV/Vis (acetone) λ_{max} [nm] ($\log\varepsilon$): 326 (4.13), 366 (3.91), 652 (3.90), 668 (4.05); FT-IR (NaCl, cm^{-1}): $\tilde{\nu}_{CO} = 1698$; 1524 (w), 1456 (w), 1287 (s), 1250 (s), 1214 (s), 1168 (s), 1155 (s), 1109 (s), 1097 (s), 975 (w), 959 (w), 723 (s). The ESR spectrum exhibits the expected[23] multiline pattern for a Co^{II} center with a singly-occupied d_{z^2} orbital: $g_{\parallel} = 2.008$, $g_{\perp} = 2.217$.[24] The sample submitted for microanalysis was recrystallized from methanol, elemental analysis: calcd (%) for $CoC_{58}H_8N_8O_2F_{64}$, ($CoC_{56}N_8F_{64} \cdot 2$ methanol): C 32.80, H 0.38, N 5.28; found: C 32.52, H 0.56, N 5.27.

2: Excess triphenylphosphane was added to **1** (0.016 g, 0.0074 mmol) in acetone (10 mL). After 5 min, thin-layer chromatography (TLC), UV/Vis and IR spectroscopy indicated that the reaction was complete. No unreacted **1** was observed. UV/Vis (acetone) λ_{max} [nm] ($\log\varepsilon$) 330 (4.88), 422 (4.50), 476 (4.42), 582 (4.60), 710 (4.74); FT-IR (NaCl, cm^{-1}): $\tilde{\nu}_{CO} =$ 1509 (s); 1436 (s), 1405 (s), 1250 (s), 1213 (w), 1166 (w), 1111 (w), 974 (w), 956 (w), 751 (s), 722 (s), 694 (s), 541 (s); ^{31}P NMR (121.495 mHz, $[D_6]$acetone, H_3PO_4) $\delta = 15.53$ (for the uncoordinated ylide). Elemental analysis: calcd (%) for $CoC_{98}H_{38}N_8O_2F_{64}P_2$: C 43.66, H, 1.42, N 4.16; found: C 43.51, H 1.41, N 4.29. X-ray quality crystals were grown by the slow evaporation of the solution in air. About 10% triphenylphosphane oxide (relative to the ylide) was produced along with **2** in a parallel reaction, consistent with the observations that triphenylphosphane oxide is produced in toluene from Ph_3P and air in the presence of acetone-depleted $[F_{64}PcCo]$. Triphenylphosphane oxide does not react separately with acetone in the absence or presence of $[F_{64}PcCo]$, and thus it is not an intermediate on the reaction path to 1-triphenylphosphoranylidene-2-propanone.

3: A 200-fold excess of tributylphosphane, (0.5 mL, 2.007 mmol) was added to **1** (0.020 g) in acetone (50 mL). A purple color developed immediately. UV/Vis (acetone) λ_{max} [nm] (($\log\varepsilon$) 340 (4.77), 426 (4.48), 474 (4.45), 578 (4.62), 710 (4.76); MS (FAB, NBA): 2577 $[M{+}1]$. Addition of excess acetone to **3** resulted in the regeneration of **1** in quantitative yield, as judged by UV/Vis spectroscopy, and free 1-tributylphosphoranylidene-2-propanone. GC-MS: 257 $[M^{+}]$.

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Observation of Uniaxial Negative Thermal Expansion in an Organic Crystal**

Henrik Birkedal,* Dieter Schwarzenbach, and Philip Pattison

In the past few years, crystal engineering has attracted ever-increasing interest.[1] This subject is concerned with the design of solids with specific, controlled properties. One such coveted property is negative thermal expansion (NTE). Several inorganic systems exhibiting NTE are known[2–4] but organic materials displaying NTE have very rarely been reported.[5] Here we show that the monohydrate of the dipeptide tryptophylglycine[6] (TrpGly · H_2O) crystallizes in a supramolecular helix that extends throughout the entire crystal, thus forming a peptide nanotube,[7] and that the thermal expansion along the helical axis is negative below room temperature.

The crystal structure of TrpGly · H_2O was investigated at 295 and 120 K using bending magnet synchrotron radiation at the Swiss–Norwegian Beam Line (SNBL at ESRF, France).[8] The single-crystal sample had dimensions $20 \times 30 \times 180$ µm^3. In spite of the small size, data of high quality could be collected and refinements proceeded to an R_1(all) below 3.2% at both temperatures. The molecular structure is shown in Figure 1.

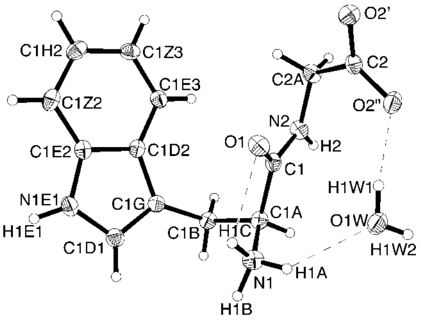

Figure 1. Structure of TrpGly · H_2O as determined at 120 K. Displacement ellipsoids are drawn at the 50% probability level. Only the majority water site is shown. Hydrogen atoms involved in conventional hydrogen bonds are labeled. Dashed lines indicate hydrogen bonds.

The crystal structure is tetragonal and the peptide forms a helical structure parallel to the *c* axis. This helix, Figure 2, encloses a channel in which the water molecules are located. The peptide channel extends throughout the entire crystal and has approximate internal dimensions of 8.3×8.3 Å^2. The van der Waals accessible volume[9] is 80.5 and 76.8 Å^3 per unit cell at 295 and 120 K, respectively. The peptide helix thus forms a peptide nanotube occupied by water molecules. The

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