Host–Guest Chemistry

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Mechanism of Host–Guest Complex Formation and Identification of Intermediates through NMR Titration and Diffusion NMR Spectroscopy**

*Jan-Hendrik Lamm, Philipp Niermeier, Andreas Mix, Jasmin Chmiel, Beate Neumann, Hans-Georg Stammler, and Norbert W. Mitzel**

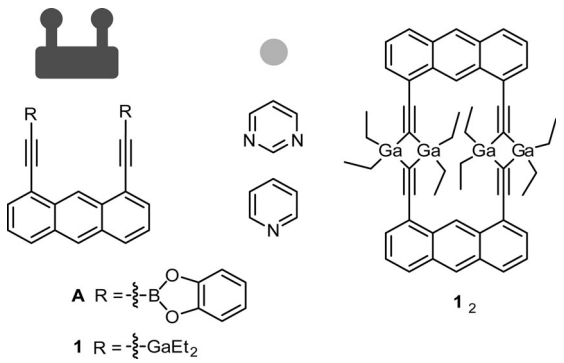
Dedicated to Professor Lothar Weber on the occasion of his 70th birthday

Abstract: *The formation of host–guest (H-G) complexes between 1,8-bis[(diethylgallanyl)ethynyl]anthracene (H) and the N-heterocycles pyridine and pyrimidine (G) was studied in solution using a combination of NMR titration and diffusion NMR experiments. For the latter, diffusion coefficients of potential host–guest structures in solution were compared with those of tailor-made reference compounds of similar shape (synthesized and characterized by NMR, HRMS, and in part XRD). Highly dynamic behavior was observed in both cases, but with different host–guest species and equilibria. With increasing concentrations of the pyridine guest, the equilibrium* $H_2 \rightleftarrows H_2\kappa^1\text{-}G_1 \rightleftarrows HG_2$ *is observed (in the second step a host dimer coordinates one guest molecule); for pyrimidine the equilibrium* $H_2 \rightarrow H_1\kappa^2\text{-}G_1 \rightleftarrows HG_2$ *is observed (the formation of a 1:1 aggregate is the second step).*

Host–guest chemistry has become a well-established part of macromolecular chemistry since Pedersen reported the formation of potassium crown ether complexes in 1967.[1] Today more than 5000 crown compounds are known.[2] Their complexation principle was extended to three-dimensional host systems such as cryptands.[3] In contrast to this well-understood and extensively studied cation complexation (Lewis acids) by poly-Lewis bases, the inverse situation with poly-Lewis acids as host compounds is less well explored. This might be due to the high reactivity of many Lewis acidic compounds and a distinct paucity of donor-free frameworks to carry suitable Lewis acid functions. Known examples of such host systems include species based on silicon,[4] tin,[5] mercury[6] as well as boron,[6d,7] aluminum,[8] gallium,[8c,d,9] and indium[10] as Lewis acid functions.

Common to most examples are acid functions attached to a more or less flexible organic framework. Flexible receptors are capable of binding a wide range of guest species, but this flexibility is equipollent to low selectivity. However, there are also some systems with rigid frameworks. For instance the rigid 1,2-bis(organostannyl)benzene hosts have been demonstrated to be superior fluoride acceptors[11] than the less rigid methylene- and dimethylene-bridged bisstannanes.[12] Similar results exist for 1,2-disilylbenzenes[13] and 1,8-naphthalenediboranes.[14] Other examples of rigid bis-Lewis acids are the 1,2-dimercuriobenzenes[15] and a 1,8-biphenylene-based tetragallium compound.[9e]

Recently, we reported the double metalation of 1,8-diethynylanthracene through alkane-elimination reactions by conversion of the corresponding dialkynes with ER_3 [with E = Al, Ga (**1**), In; R = Me, Et]. In their crystals these metalated compounds are dimers linked by [≡C(E)$_2$C≡] units (Scheme 1).[16]



Scheme 1. The anthracene-based bidentate boron Lewis acid **A**[7a] and the digallium compound **1**,[16] as well as schematic representations of host and guest molecules and the dimeric structure of host compound **1** in the solid state (right).

1,8-Substituted anthracenes provide rigid organic frameworks with the opportunity to orientate reactive sites in a defined direction. Their use as receptor molecules in host–guest experiments was first explored by Katz in 1989.[7a] His bidentate boron Lewis acid **A** (Scheme 1, B···B distance ca.

[*] M. Sc. J.-H. Lamm, B. Sc. P. Niermeier, Dr. A. Mix, Dr. J. Chmiel, B. Neumann, Dr. H.-G. Stammler, Prof. Dr. N. W. Mitzel
Lehrstuhl für Anorganische Chemie und Strukturchemie
Universität Bielefeld, Fakultät für Chemie
Universitätsstrasse 25, 33615 Bielefeld (Germany)
E-mail: mitzel@uni-bielefeld.de
Homepage: http://www.uni-bielefeld.de/chemie/arbeitsbereiche/ac3-mitzel/

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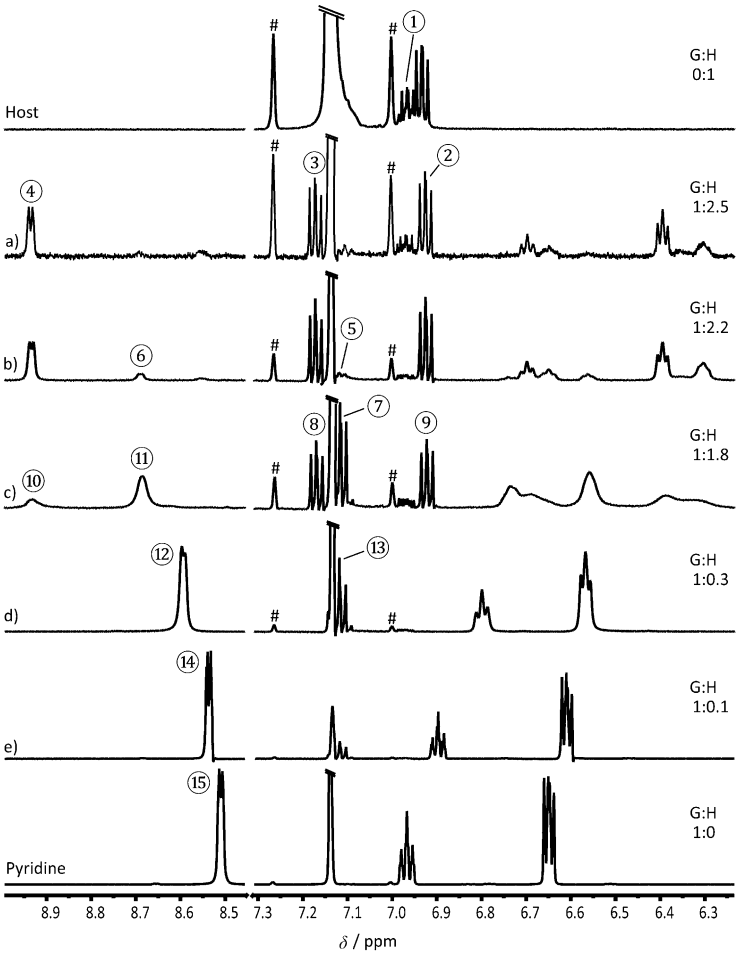


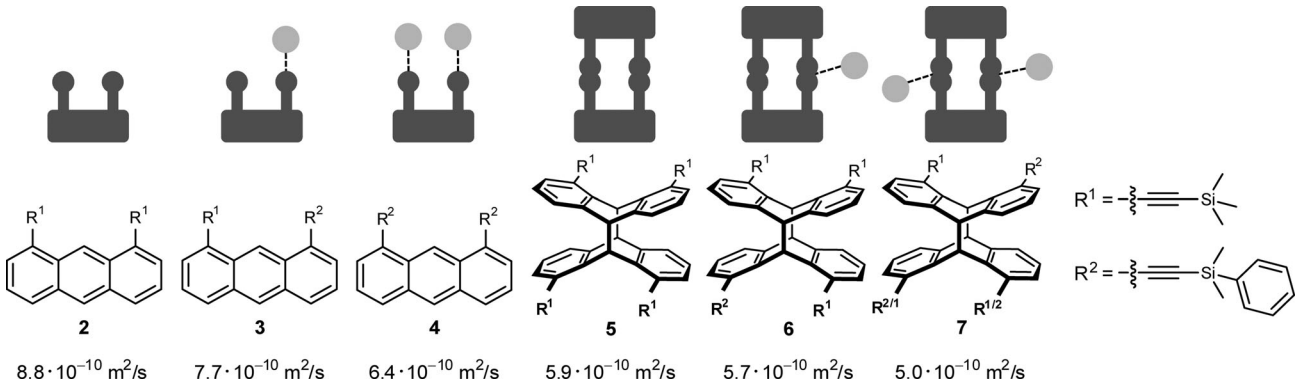
Figure 1. ^{1}H NMR spectra (600 MHz, 294 K) of host compound **1**, different host–pyridine mixtures, and pure pyridine in C_6D_6 ($\delta = 7.13$ ppm); # denotes ^{13}C satellites of C_6D_6 (cut-off signal).

5 Å) forms complexes with methylpyrimidine derivatives and has been studied by NMR titration experiments, but the results were derived from very small changes in ^{1}H NMR shifts (max. $\Delta\delta = 0.08$ ppm) of the host component.[7a]

During our studies of the formation of host–guest complexes with the digallium compound **1** we regularly observed complex ^{1}H NMR spectra like those shown in Figure 1c). On first glance these seemed to be poor in information. This raised doubts that the adduct formation proceeded as simply as previously assumed and that **1** behaved as a chelating Lewis acid as described for compound **A**. Though the isolation of a product by crystallization might be desirable for structure elucidation in this context, it would not inevitably be a good model for the solution state, the most relevant for molecular recognition. Because simple titration experiments (with pyridine: Figure 1) were not conclusive, the situation demanded a more sophisticated approach of analysis.

We found that the combination of NMR titration with diffusion NMR experiments is a novel methodological approach to characterize host–guest complexes in solution. Diffusion NMR methods are powerful tools for the analysis of compound mixtures in solution by pulsed field gradient techniques. They are applied in areas such as molecular-size determination[17] and for elucidating reaction mechanisms,[18] sodium dodecylsulfate micelle–peptide association,[19] and other complexation phenomena in solution.[20] During diffusion NMR experiments field gradients along the z-axis allow for spatially selective spin-labeling and after time-dependent detection, diffusion coefficients D can be extracted individually for every compound in a mixture. According to the Stokes–Einstein equation, D is reciprocally proportional to the hydrodynamic radius r_s, that is, the size of the molecule in solution.[21]

However, the self-translational diffusion coefficients D are strongly dependent on the shape and size of the investigated systems. For a thorough interpretation of the hydrodynamic radius value it is therefore necessary to compare the results with values of suitable model systems, preferably of well-known shape similar to that of the analytes and under the same experimental conditions. Consequently, the most time-consuming part of this work was the syntheses of such reference compounds with suitable geometry to model a couple of possible host aggregates and host–guest complexes. They are



Scheme 2. Possible host aggregates and host–pyridine structures in solution (top) and the corresponding reference compounds with their diffusion coefficients D, measured in C_6D_6 at 294 K (bottom). From left to right: H_1, H_1G_1, H_1G_2, H_2, H_2G_1, H_2G_2 with H: **1**; G: pyridine. The models also serve for the complexation of pyrimidine.

shown in Scheme 2; their syntheses are briefly outlined in reference [22] and in detail in the Supporting Information.

Figure 1 shows the changes in the ^{1}H NMR spectra of mixtures of the digallium compound **1** (host, H) with increasing concentrations of pyridine (guest, G) as well as spectra of pure H and G solutions. Due to the poor solubility of **1** in [D_6]benzene the reactant ratios in solution were measured by integration of the NMR signals. An assignment of resonances to host–guest complexes was undertaken by determination of the diffusion coefficients D associated with each signal. Scheme 2 provides a correlation of these diffusion coefficients with reference structures. The following description starts with host compound **1** and follows the changes in the spectra upon addition of increasing amounts of pyridine.

The ^{1}H NMR spectrum of the pure host **1** shows doublets of doublets, induced by the anthracene protons H3 and H6 at $\delta = 6.92$ ppm (signal labeled ②). Note that this spectrum of the sparingly soluble **1** contains enriched traces of non- and monometalated 1,8-diethynylanthracene [signals at $\delta =$ 6.97 ppm (①)] due to their better solubility; the purity of **1** determined by ^{1}H NMR analysis in [D_8]THF solution was better than 99%. The diffusion coefficient of **1**, $D = 5.9 \times 10^{-10}\,m^2s^{-1}$, is the same as that of reference compound **5** ($D = 5.9 \times 10^{-10}\,m^2s^{-1}$), but markedly deviates from that of **2** ($D = 8.8 \times 10^{-10}\,m^2s^{-1}$), the reference for a monomeric host structure. This proves that host **1** exists as dimers in benzene solution as well as in the solid state.[16]

The addition of a small amount of the guest pyridine (molar ratio G/H = 1:2.5) leads to a new doublet of doublets at $\delta = 7.17$ ppm (③) and to significantly shifted pyridine resonances. This corresponds to the formation of a new anthracene-containing pyridine complex. Its diffusion coefficient measured at signal ③ at $D = 5.8 \times 10^{-10}\,m^2s^{-1}$ is almost identical to that of host dimer H_2 (note that the estimated error in D is about $0.1 \times 10^{-10}\,m^2s^{-1}$). The fact that it is a new compound and the tendency to a smaller D indicates that this species should be slightly larger than that of the host dimer H_2. If one compares this value to the diffusion coefficients of reference compounds H_1G_1 (**3**, $7.7 \times 10^{-10}\,m^2s^{-1}$), H_1G_2 (**4**, $6.4 \times 10^{-10}\,m^2s^{-1}$), and H_2G_2 (**7**, $5.0 \times 10^{-10}\,m^2s^{-1}$) this adduct is likely to consist of one pyridine guest molecule associated with a host dimer (H_2G_1 structure). Further support for this argument is the D value of reference **6** ($5.7 \times 10^{-10}\,m^2s^{-1}$), which is the closest match. Additional confirmation stems from the diffusion coefficient of signal ④ ($6.0 \times 10^{-10}\,m^2s^{-1}$) belonging to the *ortho*-protons of pyridine. It is significantly different from that of free pyridine ⑮ ($22.1 \times 10^{-10}\,m^2s^{-1}$), but in good agreement with that of ③ ($5.8 \times 10^{-10}\,m^2s^{-1}$) and that of H_2G_1 reference **6**. It demonstrates that this pyridine unit belongs to the H_2G_1 structure. The slightly higher D value measured at resonance ④ is explicable by rapid dissociation. Due to the excess of host, the majority of pyridine is present in a bound state on time average so that the diffusion coefficient of the free pyridine contributes only to a small extent. The presence of this complexation dynamics was proven by variable-temperature (VT) NMR measurments of a 1:4 mixture of **1** and pyrimidine in [D_8]toluene with no indication of a second set of guest resonances at temperatures as low as 203 K (for details see the Supporting Information).

In Figure 1b the G/H ratio is slightly increased to 1:2.2. Under these conditions resonance ⑤ of a new host–guest species is observed. Also observed is a new set of pyridine resonances (⑥), which again shifted far downfield relative to that of free pyridine. These new resonances become much more intense when the G/H ratio is increased to 1:1.8 (Figure 1c). Under these conditions signal ⑦ at $\delta =$ 7.12 ppm ($D = 6.3 \times 10^{-10}\,m^2s^{-1}$) belongs to the main component in the mixture besides H_2G_1 (⑧ and ⑩) and the host dimer H_2 (⑨). The D value of signal ⑦ is similar to that determined for reference **4** ($6.4 \times 10^{-10}\,m^2s^{-1}$) and makes an H_1G_2 structure the most likely assignment. The addition of an excess of pyridine (Figure 1d,e) leaves the H_1G_2 complex as the only remaining host-containing species in solution (⑬).

Up to this point the analysis has been based primarily on the host signals; further support is gained by analysis of the guest signals. Thus we observed that with increasing pyridine content in the mixture, the D values of the guest increase continuously. For signal ⑩ in the mixture with G/H = 1:1.8 (Figure 1c) a value of $6.8 \times 10^{-10}\,m^2s^{-1}$ was measured, similar to that in Figure 1a. The new pyridine signal ⑪ occurring at $\delta = 8.69$ ppm at higher concentrations has a larger D value of $7.5 \times 10^{-10}\,m^2s^{-1}$. This indicates the formation of a species with smaller hydrodynamic radius r_s. Upon further addition of pyridine, just one set of guest signals remains observable (Figure 1d,e). The corresponding diffusion coefficients increase from $10.5 \times 10^{-10}\,m^2s^{-1}$ (⑫) to $18.0 \times 10^{-10}\,m^2s^{-1}$ (⑭) and approach the value of noncomplexed pyridine (⑮, $22.1 \times 10^{-10}\,m^2s^{-1}$). As there is still rapid exchange between the host–guest complex and free pyridine, the unbound pyridine available in the mixture contributes increasingly to the measured diffusion coefficient. This is because only a mean value weighted by the molar fractions is observable on the timescale of the NMR experiment.

We also used pyrimidine as a guest exhibiting two donor atoms to investigate the Lewis base complexation of host **1**. In contrast to the addition of pyridine and in analogy to the results postulated by Katz in 1989,[7a] we expected the formation of an H_1G_1 structure (Scheme 2) with pyrimidine bound in a chelating fashion through two Ga–N bonds. This should particularly be the case, when small amounts of pyrimidine are added to the bidentate host molecule **1**. In fact, completely different behavior was observed when pyrimidine was added instead of pyridine (see Table 1).

Upon addition of a substoichiometric amount of pyrimidine (molar ratio G/H = 1:1.17) the formation of only one anthracene-containing complex with a diffusion coefficient of $7.2 \times 10^{-10}\,m^2s^{-1}$ was observed. If one compares this to the D values of the reference compounds H_1G_1 (**3**, $7.7 \times 10^{-10}\,m^2s^{-1}$), H_2G_1 (**6**, $5.7 \times 10^{-10}\,m^2s^{-1}$, the intermediate analogue to substoichiometric conversion of **1** with pyridine), and H_2G_2 (**7**, $5.0 \times 10^{-10}\,m^2s^{-1}$), the formation of a complex consisting of a host monomer and one pyrimidine molecule (H_1G_1 structure with chelating bound pyrimidine) is most likely (the small deviation of the D value from that of reference **3** may be due to the fact that **3** represents a monodentate-bound pyrimidine aggregate). This complex is apparently very stable, because we do not observe any other anthracene-containing species when the pyrimidine concen-

Table 1: Selected results from diffusion NMR experiments for various mixtures of **1** and pyrimidine.[a]

G/H	*D* (host)[b]	*D* (guest)[b]
1:1.17	6.9	7.2
1:1.14	6.9	7.1
1:1.10	7.1	7.2
1:0.38	7.0	13.7
1:0.16	6.8	17.9
1:0.06	6.6	19.9

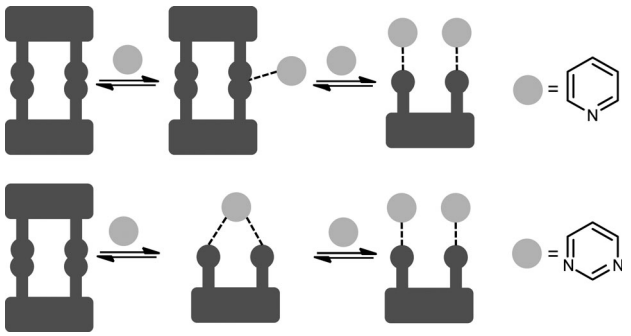
[a] For complete data see Table S5 in the Supporting Information. [b] *D* [10^{-10} $m^2 s^{-1}$] measured in C_6D_6 at 294 K.

tration is increased. The diffusion coefficients measured for the single set of guest ^{1}H NMR resonances are very similar to those determined for the host signals, when the mixture contains an excess of host. Addition of further quantities of pyrimidine (G/H = 1:0.38 and higher) leads to an increase of the guest's diffusion coefficients (see Table 1). Like in case of pyridine complexation described above, the *D* values continuously approach the value of free pyrimidine ($D = 20.7 \times 10^{-10}$ $m^2 s^{-1}$), again reflecting the exchange of free and bound guest.

However, the diffusion coefficients for the host compound tend to decrease when an excess of pyrimidine is used; this is possibly due to formation of some H_1G_2 structure (reference compound **4**: $D = 6.4 \times 10^{-10}$ $m^2 s^{-1}$), whereby each pyrimidine would use only one nitrogen atom for binding to the host.

In summary, the bidentate Lewis acid **1** behaves very differently in the complexation of the mono- and difunctional N-heterocyclic guest molecules pyridine and pyrimidine. The complexation by pyridine turned out to be far more complex than anticipated and involves previously unpredicted species. Although the use of a combination of NMR titration and diffusion NMR spectroscopy in a dynamic system does not allow determining exact structures, the composition and tentative structure assignment can be extracted from the experimental data. Scheme 3 compiles the results in graphical form.

Pyridine is first complexed to the host dimer, then this aggregate is cleaved to give a complex of one host and two pyridine units; in a certain regime of concentrations these species are found to coexist. For pyrimidine, there is no experimental proof for a similar aggregate consisting of a host dimer and one pyrimidine molecule. Instead almost immediate formation of a (possible) chelate between the difunctional host and one guest is observed. This H_1G_1 species remains the dominant species even under higher guest concentrations, while there is some evidence for the formation of small amounts of a complex of two pyrimidine units bound to one host molecule (H_1G_2 species).



Scheme 3. Different complexation phenomena when pyridine (top) and pyrimidine (bottom) are used as guest compounds.

In general, the combination of titration and diffusion NMR experiments allows new insights in the chemistry of molecular recognition by chelating Lewis acids, provided one is able to compare diffusion coefficients with those of suitable tailor-made reference compounds. The method combination can be transferred to other complex aggregation phenomena.

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[22] Reference compounds **2**–**4** (Scheme 2) were synthesized in good to moderate yields by Ni-catalyzed Kumada cross-coupling reactions using [(trimethylsilyl)ethynyl]magnesium bromide and {[dimethyl(phenyl)silyl]ethynyl}magnesium bromide,[23] respectively, to functionalize 1,8-dichloroanthracene.[16,24] Compounds **2**–**4** were characterized by multinuclear NMR spectroscopy as well as mass spectrometry and in part by X-ray diffraction experiments. The host dimer reference **5** was obtained by photodimerization (365 nm) of **2** in C_6D_6 solution, whereas H_2G_2 (**7**) and H_2G_1 (**6**) compounds were generated by irradiating NMR samples of pure **3** and a 1:1 mixture of **2** and **3**, respectively. Compounds **5**–**7** were not isolated in pure form, and solely generated to determine their diffusion coefficients. In this case, the diffusion coefficient of the asymmetrically substituted **3** can be compared with the H_1G_1 structure (one N-heterocyclic guest molecule coordinates to one host monomer **1**), whereas **4** serves as a model system for the H_1G_2 structure. Compound **2** represents a monomeric host structure (**H_1**) and **5** (obtained by UV irradiation of **2**) is used as a reference for a dimeric host structure (H_2) which has been observed in the solid state (see Ref. [16]).
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