

Synthesis and Spectroscopic Characterization of New Molecular Complexes of Bismuth(III) Chloride with Free Base *meso*-Tetraarylporphyrins

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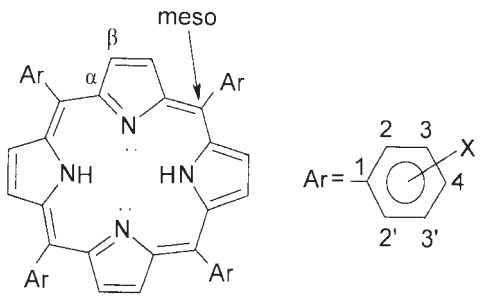
Reaction of bismuth(III) chloride ($BiCl_3$) with free base *meso*-tetraarylporphyrins ($H_2t(X)pp$, X = 4-Me, 4-OMe, 3-Me, 3-OMe, and H) in $CHCl_3$ under mild conditions gives exclusively 1:1 molecular complexes with the general formula $[(BiCl_3\{H_2t(X)pp\})_2]$. The remarkable agreement between ^1H and ^{13}C NMR and UV–vis spectra of the porphyrin macrocycle in these complexes and those of *meso*-tetraarylporphyrin molecular complexes with DDQ, TCNE, SiR_3Cl, and BF_3 indicates that they all have a similar porphyrin core. The molecular complexes have a dimer structure containing a Bi_2Cl_6 moiety. In the proposed structures for the complexes, four pyrroles are tilted alternatively up and down with respect the porphyrin mean plane, which leads to the appropriate orientation of the nitrogen lone pairs towards the central bismuth atoms. Therefore, octahedral geometry for the bismuth center is proposed.

Interaction of free base porphyrins with acceptors has been the subject of some recent investigations.[1–5] It has been shown that porphyrins are only capable of forming 1:2 molecular complexes with π- or σ-acceptors.[1–5] Bismuth(III) porphyrins have not been studied extensively. In all synthesized complexes, an anionic porphyrin moiety (por^{2-}) ligate to the metal center as a tetradentate ligand so that they no longer may be considered as molecular complexes of porphyrins with bismuth(III) chloride.[6] Recently, it has been demonstrated that the reaction of $BiCl_3$ and free base porphyrin in dry pyridine, after 12 h of refluxing, led to the formation of the [{Bi(t*p*Clpp)Cl}$_2$] (t*p*Clpp = 5,10,15,20-tetra-*p*-chlorophenylporphyrin) complex. The molecular structure reported for this complex shows that the complex crystallizes as centrosymmetric dimer doubly bridged by Cl. In this compound, both hydrogen atoms of the central pyrrole NH groups of porphyrin are lost, and the bismuth atoms are significantly displaced from the porphyrin N_4 plane. In the complex, the bismuth atoms are hexacoordinate.[7]

This work presents for the first time 1:1 molecular complexation of various *meso*-tetraarylporphyrins, $H_2t(X)pp$, (Fig. 1) with $BiCl_3$ that produced dimer $[(BiCl_3\{H_2t(X)pp\})_2]$ molecular complexes. Based on the ^1H and ^{13}C NMR and UV–vis spectra, which resembles those of the related molecular complexes with DDQ (2,3-dichloro-5,6-dicyanobenzoquinone), TCNE (tetracyanoethylene), SiR_3Cl, and BF_3, the complexes have saddled porphyrin core structures with one $BiCl_3$ molecule bonded to two pyrrolic nitrogens above or below the porphyrin plane.[1–4]



X = 4-Me, $H_2t(4\text{-Me})pp$

X = 4-OMe, $H_2t(4\text{-OMe})pp$

X = 3-Me, $H_2t(3\text{-Me})pp$

X = 3-OMe, $H_2t(3\text{-OMe})pp$

X = H, H_2tpp

Fig. 1. *meso*-Tetraarylporphyrins, $H_2t(X)pp$.

Results and Discussion

Figure 2 shows the ^1H NMR spectra of $H_2t(4\text{-Me})pp$ (Fig. 2a) and its molecular complexation with $BiCl_3$ (Fig. 2b). If the amount of $BiCl_3$ is less than $H_2t(4\text{-Me})pp$, the spectra of the porphyrin and related molecular complex appear superimposed, while an excess amount of $BiCl_3$ caused no changes in the spectra of the 1:1 molecular complex. Consequently, the molecular complex between $H_2t(4\text{-Me})pp$ and $BiCl_3$ has a 1:1 ratio. The reaction of $BiCl_3$ with $H_2t(4\text{-Me})pp$, similar to 1:2 (donor:acceptor) complexation[1–3] and diprotonation of *meso*-tetraarylporphyrins,[8] causes an upfield shift in the β-protons (0.26 ppm) and downfield shifts in the NH signal (3.18 ppm) and *meso*-aryl-substituted signals (Table 1). The interaction of other *meso*-tetraarylporphyrins (Table 1) with $BiCl_3$, similar to the molecular complexation of the *meso*-tetraarylporphyrins by DDQ,[1] TCNE,[2] and SiR_3Cl[3] caused a downfield shift in NH signals (3.02–3.36 ppm) and the signals of aryl ring protons and an upfield shift in the β-hydrogens (0.23–0.34 ppm, Table 1). The shifts in N–H and β-protons are subject to the ring current in the free base porphyrin and

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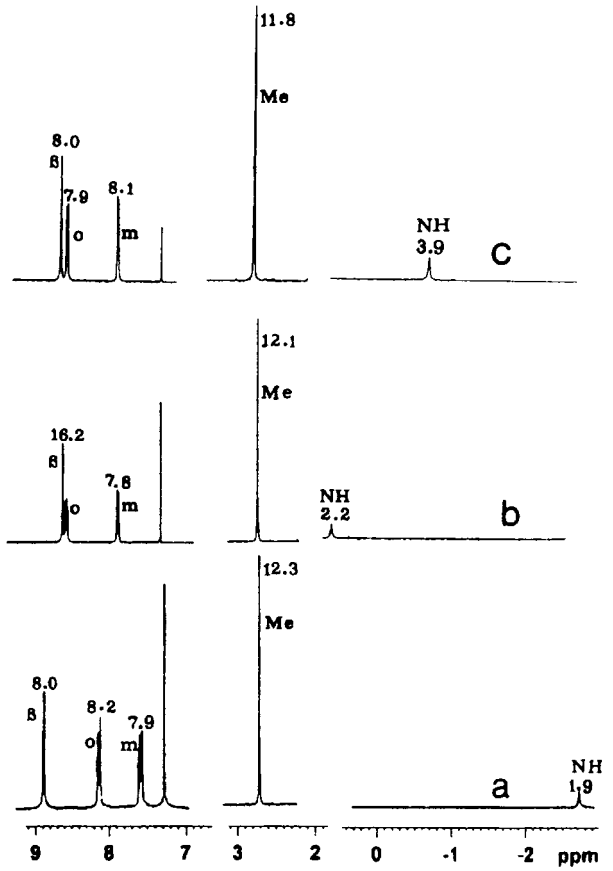

Fig. 2. ^{1}H NMR spectra (500 MHz) of (a) H_2t(4-Me)pp, (b) [($BiCl_3${H_2t(4-Me)pp})$_2$] molecular complex, and (c) H_4t-(4-Me)pp^{2+}. Line at 7.27 ppm region is related to $CHCl_3$ in the solvent.

the molecular complexes. Saddling of the porphyrin core should lead to a decrease in the ring current. The molecular complexation of the porphyrins caused downfield shifts in the aryl ring protons. This might result from a direct increase in ring current of aryl groups produced by extension of the aryl π-system.[1–3,8]

The ^{1}H NMR spectrum of the molecular complexes of *meso*-tetraarylporphyrins with various acceptors (DDQ, TCNE, SiR_3Cl, and BF_3) resembles the ^{1}H NMR spectrum of the related diprotonated porphyrin species.[1–4] The ^{1}H NMR spectrum of H_4t(4-Me)pp^{2+} is shown in Fig. 2c. The ^{1}H NMR spectrum of the H_4t(4-Me)pp^{2+} was quite sensitive to the concentration of CF_3COOH,[4] but an excess of $BiCl_3$ had no effect on the ^{1}H NMR spectrum of the [($BiCl_3${H_2t(4-Me)pp})$_2$]. Furthermore, the integration of the pyrrolic NH hydrogen peak in 0.006 M $CDCl_3$ solution of the [($BiCl_3${H_2t(4-Me)pp})$_2$] molecular complex was 2.2 (Fig. 2b), whereas for the H_4t(4-Me)pp^{2+} it was 3.9 (Fig. 2c). In other words, a diprotonated porphyrin species cannot form in our reaction system. The remarkable spectral correspondence between the [($BiCl_3${H_2t-(4-Me)pp})$_2$] and H_4t(4-Me)pp^{2+} suggested analogous saddled porphyrin core structures and π-system in these species.[8]

The ^{13}C NMR spectrum of H_2t(4-Me)pp has six signals in the aromatic region: one broad signal for β-carbons (131.37 ppm) and five sharp lines (C_1 = 139.73, $C_{2,2'}$ = 134.92, $C_{3,3'}$ = 127.81, C_4 = 137.71, C_{meso} = 120.47).[1,2] The α-carbons peaks at about 145 ppm are too broad and weak to be seen. ^{13}C NMR spectrum of the molecular complex between this porphyrin with $BiCl_3$ had seven signals in the aromatic region: 122.9 (C_{meso}), 128.2 (C_β), 129.6 ($C_{3,3'}$), 137.9 (C_1), 139.4 ($C_{2,2'}$), 140.7 (C_4), 146.5 (C_α). Complexation of the porphyrin with $BiCl_3$ sharpens the α and β carbon signals. On the other hand, it causes a small downfield shift in the lines of C_{meso}, $C_{2,2'}$, $C_{3,3'}$, C_4 and an upfield shift in C_β and C_1 signals. Complexation of H_2t(4-Me)pp with DDQ[1] and TCNE[2] causes the same changes in the respective ^{13}C NMR spectra.

Table 1. ^{1}H NMR Spectral Data of Different *meso*-Tetraarylporphyrins, [($BiCl_3${H_2t(X)pp})$_2$] Complexes and H_4t(4-Me)pp^{2+}

Compounds	N–H	H_β
H_2t(4-Me)pp	−2.77	8.85
[($BiCl_3${H_2t(4-Me)pp})$_2$]	0.41	8.59
$\Delta\delta_1$[a)]	3.18	−0.26
H_4t(4-Me)pp^{2+}	−0.65	8.67
$\Delta\delta_2$[b)]	2.12	−0.18
H_2t(4-OMe)pp	−2.75	8.86
[($BiCl_3${H_2t(4-OMe)pp})$_2$]	0.61	8.52
$\Delta\delta_1$[a)]	3.36	−0.34
H_2t(3-Me)pp	−2.75	8.88
[($BiCl_3${H_2t(3-Me)pp})$_2$]	0.27	8.61
$\Delta\delta_1$[a)]	3.02	−0.27
H_2t(3-OMe)pp	−2.75	8.90
[($BiCl_3${H_2t(3-OMe)pp})$_2$]	0.29	8.67
$\Delta\delta_1$[a)]	3.04	−0.23
H_2tpp	−2.76	8.85
[($BiCl_3${H_2tpp})$_2$]	0.35	8.62
$\Delta\delta_1$[a)]	3.11	−0.23

a) $\Delta\delta_1$: Chemical shifts of the proton signals for the porphyrins upon the molecular complexation. b) $\Delta\delta_2$: Chemical shifts of the proton signals for the H_2t(4-Me)pp upon the diprotonation with excess of CF_3COOH.

The UV–vis spectrum of H_2t(4-Me)pp has absorption bands at 418.3 (the soret), 518.4, 554.0, 593.0, and 649.0 nm,[1–3] whereas the molecular complex had two new absorption bands at 448.9 (soret) and 671.2 nm (Fig. 3). Upon the addition of $BiCl_3$ to free base H_2t(4-Me)pp, the UV–vis spectrum of the porphyrin is 22.2–30.6 nm red-shifted. These red shifts provide evidence for the out of plane distortion of the porphyrin core, which causes a strong interaction to occur between the aryl rings and porphyrin π-system.[1–4,8] The UV–vis spectra of $CHCl_3$ solutions of the *meso*-tetraarylporphyrins have five absorption bands in the 400–655 nm region,[1–4,8] i.e., one strong band in the 416.7–419.5 nm region is Soret, and four other weaker bands, that upon complexation with $BiCl_3$ red shifted to red and appear as two new bands in the 446.0–454.4 nm (Soret band) and in the 660.1–690.6 nm regions, as listed in Table 2. The red shift for the [($BiCl_3${H_2t(X)pp})$_2$] complex was more than other studied molecular complexes.

The UV–vis spectra of the [($BiCl_3${H_2t(X)pp})$_2$] complexes are closely related to the UV–vis spectra of H_4t(X)pp^{2+} (Fig. 3 and Table 2). An excess of $BiCl_3$ had no effect on the UV–vis spectrum of the [($BiCl_3${H_2t(X)pp})$_2$] complex while the spec-

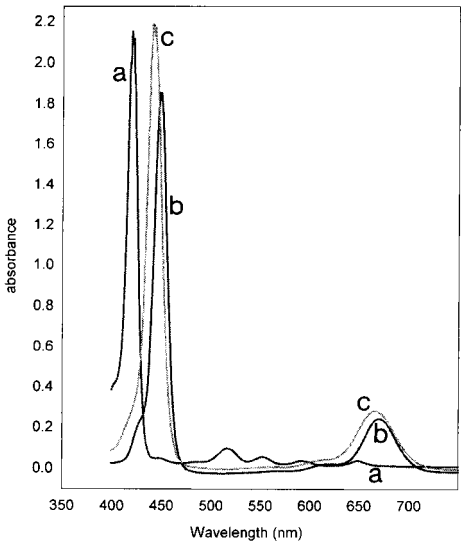

Fig. 3. UV–vis spectra of (a) $H_2t(4\text{-Me})pp$, (b) $[(BiCl_3\{H_2t(4\text{-Me})pp\})_2]$ molecular complex, and (c) $H_4t(4\text{-Me})pp^{2+}$ in $CHCl_3$.

Table 2. UV–Vis Spectral Results of the Different *meso*-Tetraarylporphyrins, $[(BiCl_3\{H_2t(X)pp\})_2]$ Complexes, and Their Diprotonated Species in $CHCl_3$

Compounds	λ_{max}/nm	
	Peaks	
$H_2t(4\text{-Me})pp$	418.3(S), 518.4, 554.0, 593.0,	649.0
$[(BiCl_3\{H_2t(4\text{-Me})pp\})_2]$	448.9(S)	671.2
$\Delta\lambda_1$ [a]	30.6	22.2
$H_4t(4\text{-Me})pp^{2+}$ [c]	442.2(S)	663.4
$\Delta\lambda_2$ [b]	23.9	14.4
$H_2t(4\text{-OMe})pp$	419.5(S), 520.5, 557.1, 596.0,	653.0
$[(BiCl_3\{H_2t(4\text{-OMe})pp\})_2]$	454.4(S)	690.6
$\Delta\lambda_1$ [a]	34.9	37.6
$H_4t(4\text{-OMe})pp^{2+}$ [c]	450.0(S)	686.2
$\Delta\lambda_2$ [b]	30.5	32.8
$H_2t(3\text{-Me})pp$	418.2(S), 517.5, 550.6, 590.0,	647.2
$[(BiCl_3\{H_2t(3\text{-Me})pp\})_2]$	446.0(S)	661.1
$\Delta\lambda_1$ [a]	27.8	13.9
$H_4t(3\text{-Me})pp^{2+}$	439.4(S)	657.0
$\Delta\lambda_2$ [b]	21.2	9.8
$H_2t(3\text{-OMe})pp$	418.9(S), 517.0, 550.3, 590.3,	646.6
$[(BiCl_3\{H_2t(3\text{-OMe})pp\})_2]$	452.4(S)	660.1
$\Delta\lambda_1$ [a]	33.5	14.5
$H_4t(3\text{-OMe})pp^{2+}$	448.8(S)	657.8
$\Delta\lambda_2$ [b]	29.9	11.2
H_2tpp	416.7(S), 516.8, 551.5, 592.0,	648.0
$[(BiCl_3\{H_2tpp\})_2]$	446.1	661.2
$\Delta\lambda_1$ [a]	30.6	13.2
H_4tpp^{2+} [c]	436.1(S)	652.2
$\Delta\lambda_2$ [b]	19.4	4.2

a) $\Delta\lambda_1$: Red shifts for the bands of the porphyrins upon the molecular complexation. b) $\Delta\lambda_2$: Red shifts for the bands of the porphyrins upon the diprotonation. c) The data are taken from Ref. 4. d) (S): Soret band.

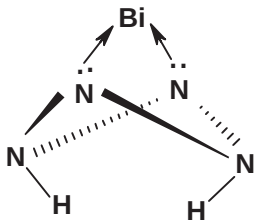

Fig. 4. The out of plane distortion of the porphyrin core causes two of the nitrogen atoms to be able to act as electron donors to a bismuth ion of $BiCl_3$.

trum of $H_4t(X)pp^{2+}$ was sensitive to additional amounts of CF_3COOH.[4] The similarity of the spectra of $[(BiCl_3\{H_2t(X)pp\})_2]$ and $H_4t(X)pp^{2+}$ suggest analogous porphyrin core structure in these species.

^1H NMR and UV–vis spectral shifts upon molecular complexation of different *meso*-tetraarylporphyrins with $BiCl_3$ indicate that π-resonance rather than σ-induction effects are predominantly transmitted from aryl substituents to the porphyrin core in the molecular complexes (Table 1 and Table 2).[1,2,8] Furthermore, steric hindrance from *meta*-substituent of the aryl rings in the porphyrins is more than from *para*-substituent and causes weaking of electron donation for *meta*-substituent. The porphyrins with *ortho*-methyl and *ortho*-methoxy substituents had no interaction with $BiCl_3$ under our experimental conditions. The trend in electron-donating ability for the substituted *meso*-tetraarylporphyrins was *para* > *meta* > *ortho*. It is noteworthy that protonation of the ortho substituents on *meso*-tetraarylporphyrins (2-Me and 2-OMe) instantly produced the corresponding green diprotonated species in $CHCl_3$. The absence of reaction between $BiCl_3$ and $H_2t(2\text{-X})pp$ clearly demonstrates the importance of the steric effects of the porphyrins in these complexation reactions.

^1H NMR, ^{13}C NMR, and UV–vis correspondences between spectral data of 1:2 (donor:acceptor) molecular complexes of σ- or π-acceptors with *meso*-tetraarylporphyrins[1–4] and $[(BiCl_3\{H_2t(X)pp\})_2]$ lead to the proposition of similar structure for porphyrin core in all of the species in which pyrrole rings are tilted alternately up and down. This conformation causes the lone pairs of two pyrrolic nitrogens to act the electron donors to one molecule of $BiCl_3$ that is located above or below the mean plane of the porphyrin, and so, the two hydrogen atoms of pyrroles (N–H) are located on the other side of the porphyrin plane (Fig. 4).

In the electrospray mass spectrum of $H_2t(4\text{-Me})pp$ and $BiCl_3$ molecular complex a peak was observed at $m/z =$ 2012.3. This was assigned the molecular complex $[(BiCl_3\{H_2t(4\text{-Me})pp\})_2]$ (MW 1971.6) and $[M + CH_3CN]$ 2012.6). The Far-IR spectrum (200–400 cm^{-1}) of the $[(BiCl_3\{H_2t(4\text{-Me})pp\})_2]$ complex showed eight bands at 331, 316, 300, 285, 267, 254, 239, and 218 cm^{-1}. The close correspondence between the vibration bands of Bi–Cl in the current molecular complex and the complexes of $BiCl_3$ with diphosphine and diarsine ligands[9] suggests that these complexes have similar structures. Consequently, the bismuth ion has an octahedral coordination geometry composed of the chelating $H_2t(4\text{-Me})pp$ ligand, two terminal Bi–Cl's and a $(\mu\text{-Cl})_2$ bridge (Fig. 5). Two vibration bands in 250–270 cm^{-1} region were assigned

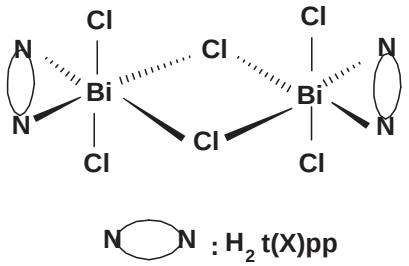

Fig. 5. Schematic representation of the [($BiCl_3${H_2t(X)-pp})$_2$] complexes. For the molecular complexes, two Bi atoms accept two electron pairs of the distorted *meso*-tetraarylporphyrins and are coordinated by two chloro bridges and two terminal Cls producing octahedral geometry.

to the chloro bridge between two bismuth atoms.[10] Furthermore, in the IR (400–4000 cm^{-1}) spectra of the free base *meso*-tetraarylporphyrins, an N–H stretching band has been observed at 3320 cm^{-1},[11] which do not change upon the reaction of the complexation with $BiCl_3$. This indicates that there is no intramolecular or intermolecular hydrogen bonding involving the N–H of *meso*-tetraarylporphyrins in the dimer molecular complexes.

A singlet for β-protons of ^{1}H NMR spectrum of *meso*-tetraarylporphyrins is in contrast to unsymmetrical pyrrole rings in the proposed structures of the molecular complexes (Fig. 2b). The ring inversion of the saddled core conformation of the porphyrin is probably fast on the NMR time scale. The low-temperature ^{1}H NMR spectrum of [($BiCl_3${H_2t(4-Me)pp})$_2$] (at $-60\,^\circ$C, in $CDCl_3$) was quite sharp and showed virtually no changes with respect to that at room temperature (20 °C). However, only upfield (-0.27 ppm) and downfield (0.05 ppm) shifts in the NH and β-protons signals, respectively were observed. It may be that the lowering of temperature caused the porphyrin core to be less flexible or less planar, i.e., with greater ring currents, the NH and β signals, shifted upfield and downfield respectively.[4]

Experimental

Benzaldehyde and the substituted benzaldehydes (2-Me, 3-Me, 4-Me, 2-OMe, 3-OMe, and 4-OMe) were obtained from Merck and were used as received. Pyrrole (Merck) was distilled before use. All of the solvents that were employed for the synthesis of the porphyrins were obtained from Merck and Fluka and were used as received. Chloroform (Merck) was dried over anhydrous calcium chloride for 3 days. The *meso*-tetraarylporphyrins were prepared and purified by the literature methods,[12] and bismuth(III) chloride were obtained from Merck and used as received. Trifluroacetic acid for the diprotonation of the porphyrins was purchased from Merck and used as received.

H_2t(X)pp (0.5 mmol) and $BiCl_3$ (0.5 mmol for H_2t(4-Me)pp and (H_2t(4-OMe)pp, and 0.6 mmol for other porphyrins) were ground together in a mortar for 30–40 min at room temperature affording the green molecular complexes. Then, hot chloroform (1 mL) was added, and the mixture was ground until complexation was complete, which was determined by the disappearance of the Soret band (≈420 nm) of the porphyrin in the UV–vis spectrum. The solvent was evaporated, and the excess $BiCl_3$ removed by washing the residue with dry acetonitrile. The complexes decomposed at 70–80 °C.

The mass electrospray spectrum of [($BiCl_3${H_2t(4-Me)pp})$_2$] (MW 1971.6) had a peak at m/z 2012.3 ([M + CH_3CN]). The results of elemental analyses for [($BiCl_3${H_2t(4-Me)pp})$_2$] complex was consistent with $C_{96}H_{76}N_8Bi_2Cl_6$ Anal. Calcd: C, 58.48; H, 3.85; N, 5.68%. Found: C, 58.12; H, 3.74; N, 5.45%.

For the quantitative analysis of Cl in the [($BiCl_3${H_2t(X)pp})$_2$] compounds, 0.05 mmol of the complexes were dissolved in $CHCl_3$ (20 mL) and then decomposed by adding double distilled water (15 mL) to the solution. $BiCl_3$ hydrolyzed and the chloride ion and the porphyrin were soluble in water phase and the organic solvent, respectively. The two phases were then separated by decantation. The percentage of Cl^- ion in the molecular complex was determined by thiocyanato mercury method.[13] Anal. Calcd for $C_{96}H_{76}N_8Bi_2Cl_6$: Cl, 10.80%. Found: Cl, 10.69%.

The electronic absorption spectra were recorded in chloroform solutions on an ATI UNICAM-UV\VIS Vision SOFTWARE V-2011 spectrophotometer. The cell had an optical path length of 1 cm. The NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker 500 Ultrashield spectrometer in $CDCl_3$. To obtain good integration results in the ^{1}H NMR measurements, the concentration of the molecular complexes was 0.006 M. The residual $CHCl_3$ in the 99.8% atom $CDCl_3$ gives a signal at 7.27 ppm, which was used as a reference. The mass spectrum was recorded on a micromass LCT Mass spectrometer with Electrospray Ionization and Time of Flight Analyser in dry acetonitrile. FT-IR spectra were recorded on a Magna 550 Nicolet spectrometer using KBr pellets. Far-IR spectra were recorded on a Jasco FT/IR-680 Plus spectrometer using CsI pellets in the range of 200–600 cm^{-1}.

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