

## Solution NMR and X-Ray Structural Studies on Phthalocyaninatoiron Complexes

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Dedicated to Prof. *Giambattista Consiglio* on the occasion of his 65th birthday

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The addition of primary amines as solubilizing reagents for phthalocyaninatoiron complexes is shown to afford six-coordinate bis(amine)phthalocyaninato complexes, *i.e.*, [Fe(amine)<sub>2</sub>(pc)] **2** (amine = decan-1-amine) and **3** (amine = benzylamine), with the two new N-donors occupying the *trans*-axial positions. The new complexes were characterized by extensive NMR measurements in THF solution. For complex **3** with the benzylamine ligand, the solid-state structure was determined by X-ray diffraction methods. Complex **2** is sufficiently labile in THF solution to exchange one amine ligand against CO (gas) affording an equilibrium mixture containing [Fe(amine)(CO)(pc)] **4**.

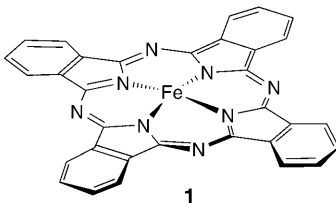
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**1. Introduction.** – It has been suggested that phthalocyaninato (pc) complexes of Fe<sup>II</sup>, [Fe(pc)]s, are attractive molecules for the development of optical sensors for detecting NO<sub>2</sub> and CO in gas samples [1–3]. The spectrum of the six-coordinated low-spin [Fe(pc)] shows an absorption maximum, λ<sub>max</sub>, at the Q-band between 655 and 670 nm [4]. The position of λ<sub>max</sub> is dependent on the donor and acceptor strength of the ligands. As a consequence of the exchange of a ligand by the specific gas molecule, the extinction at λ<sub>max</sub> decreases with the partial pressure of NO<sub>2</sub> or CO. To dissolve the potential [Fe(pc)] within a polymer film, these complexes are usually altered structurally such that their solubility in organic solvents and polymers is significantly increased. The available literature suggests that addition of dibenzylamine, decan-1-amine, or dioctylamine, amongst other reagents, accomplishes this task in that six-coordinated complexes are formed [1–6]. The ability of the phthalocyaninatometals(II) to coordinate additional ligands or solvent molecules containing N- or O-donor atoms is known [5], and solid-state structures for some few examples have been reported [6].

However, apart from optical-absorption and *Mössbauer*-spectroscopy [7] studies for these [Fe(pc)] derivatives, there are no spectroscopic data reported with respect to the coordination chemistry associated with this type of transformation. Moreover, the structure of the metal complex that evolves must be sufficiently labile such that the appropriate gas (as a ligand) can still access the metal center. To confirm the conclusions drawn from the optical spectra and to answer questions concerned with whether

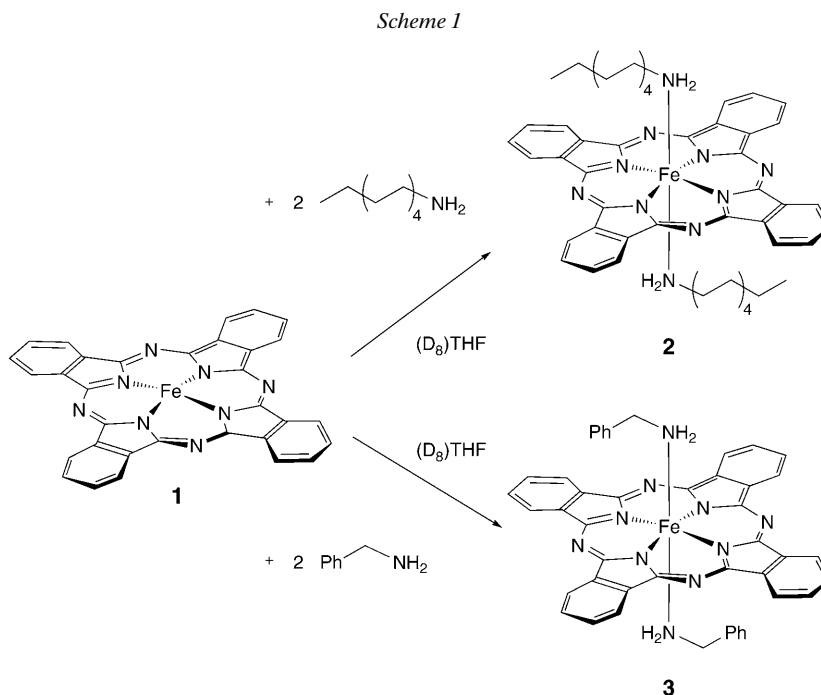
the gas molecules exchange one or both amine ligands, we have undertaken a series of NMR measurements.

We report here a solution-NMR and a solid-state study dealing with the structures of the complexes derived from the reactions of decan-1-amine and benzylamine (= benzenemethanamine) with  $[\text{Fe}(\text{pc})]$  **1**. The results show that, at least in one case, the amine complex that forms possesses the necessary lability such that a low-molecular-weight gas molecule, in our case CO, readily complexes the iron center and replaces one amine ligand at 3 bar CO pressure.



**2. Results and Discussion.** – As shown in *Scheme 1*, reaction of 2 equiv. of either decan-1-amine ( $\text{Me}(\text{CH}_2)_9\text{NH}_2$ ) or benzylamine ( $\text{PhCH}_2\text{NH}_2$ ) with  $[\text{Fe}(\text{pc})]$  **1** in THF solution affords complete conversion to the bis(decan-1-amine)- and bis(benzylamine)iron complexes **2** and **3**, respectively.

*NMR Measurements of 2 and 3.* *Fig. 1* shows the  $^1\text{H}$ -NMR spectra of the two complexes **2** and **3** in  $(\text{D}_8)\text{THF}$  solution. At 500 MHz, the various signals of the aliphatic H-



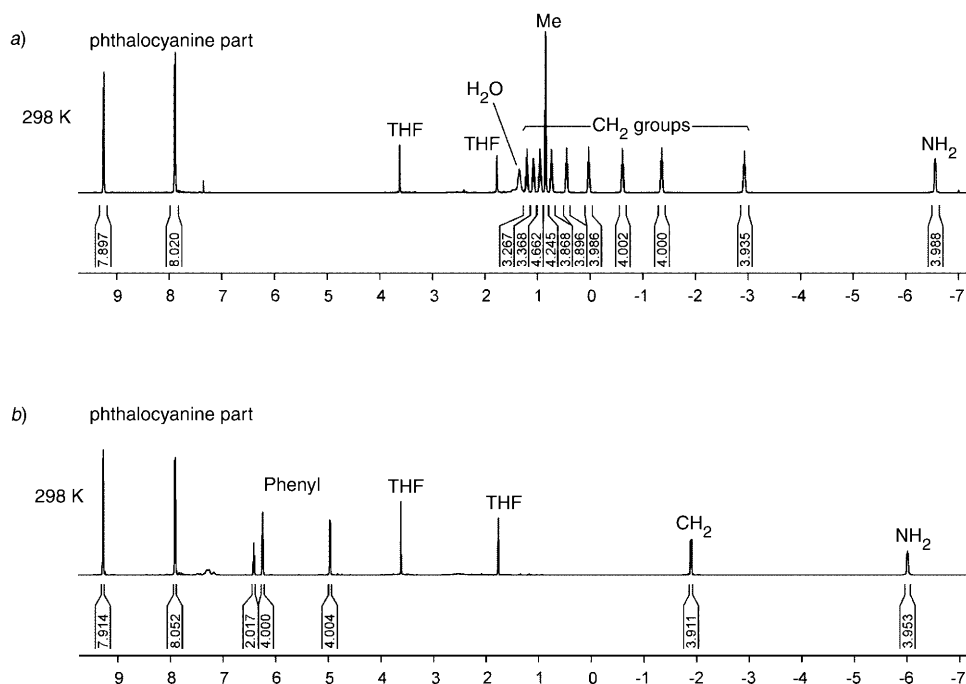


Fig. 1.  $^1\text{H}$ -NMR spectrum (500 MHz, 298 K,  $(\text{D}_8)$ THF) of a)  $[\text{Fe}(\text{decane-1-amine})_2(\text{pc})]$  **2**, and b) of  $[\text{Fe}(\text{benzylamine})_2(\text{pc})]$  **3**

atoms are well dispersed. Integration of the signals of the H-atoms in the aromatic region relative to the amine signals confirms that the new structures contain 2 equiv. of the complexed amine moieties. The interesting low-frequency signals for the amine, which appear between  $\delta$  ca. 0 and  $-7$  ppm, arise as a consequence of the local anisotropic effects associated with the phthalocyaninato structure [8]. To support this assignment, we recorded the  $^{13}\text{C}$ -NMR spectra of **2** and **3**. Fig. 2 shows the result for  $[\text{Fe}(\text{decane-1-amine})_2(\text{pc})]$  **2**. All of the observed  $^{13}\text{C}$ -NMR signals for the aliphatic part of the amine appear in relatively normal positions, *i.e.*, there are no especially low-frequency shifts since the C-atoms are much less affected by local anisotropic effects. This confirms that the observed chemical shifts do not arise from unexpected bonding modes or other phenomena.

The specific assignment of the  $\text{NH}_2$  resonances follows from two NMR experiments. In the first of these, the  $^1\text{H}$ ,  $^{13}\text{C}$ -gHMQC spectra of **2** and **3** establish that the lowest-frequency resonance ( $\delta(\text{H}) - 6.56$  for **2**) is not associated with a C,H interaction (see Fig. 3). Further, the  $^1\text{H}$ ,  $^{15}\text{N}$ -HMQC spectra of both **2** and **3** (see Fig. 4) correlate these low-frequency  $\text{NH}_2$  signals to their respective  $^{15}\text{N}$  resonances, *via*  $^1J(^{15}\text{N}, ^1\text{H})$ . Interestingly, while the  $\delta(\text{N})$  values appear in the expected region [9][10], the coupling constants  $^1J(^{15}\text{N}, ^1\text{H})$  are somewhat smaller than might be expected for a simple  $\text{sp}^3$ -hybridized N-atom [9].

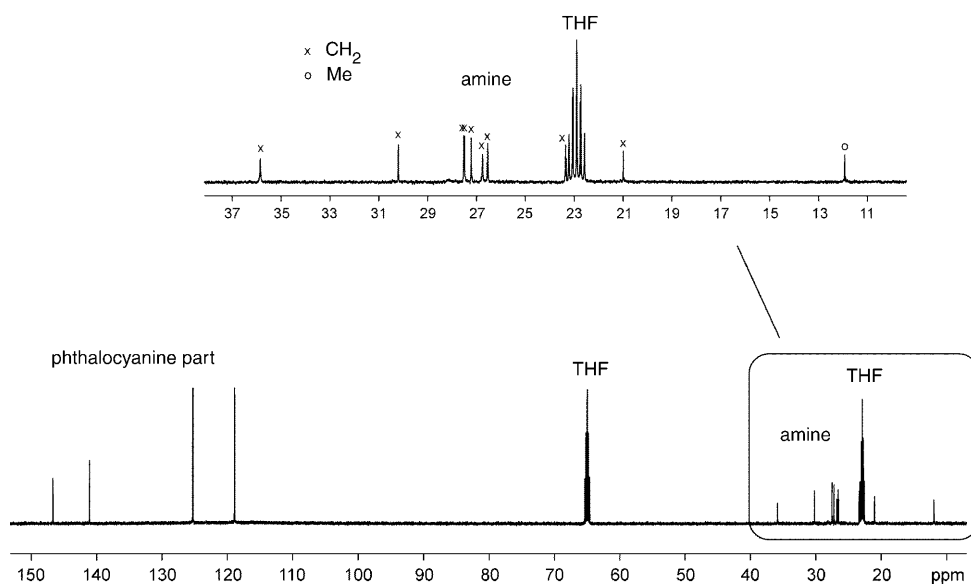


Fig. 2.  $^{13}\text{C}$ -NMR Spectrum (125.79 MHz, 298 K,  $(\text{D}_8)$ THF) of  $[\text{Fe}(\text{decane-1-amine})_2(\text{pc})]$  **2**. Top: expanded aliphatic region.

We also carried out a series of  $^1\text{H}$ -NMR measurements of **2**, between 298 and 348 K (see supplementary material<sup>1</sup>). These measurements were made with a view to probing the stability of complex **2**. Although many of the resonances broadened with increasing temperature, we found no sign of a significant amount of decomposition.

**Solid-State Structure of 3.** Crystals of the bis(benzylamine) complex **3** were obtained by slow evaporation of a THF solution. There are two independent molecules in the unit cell, one in a general position, while the other has the Fe-atom on an inversion center, thus only half of this molecule is independent. An ORTEP view of the molecule in the general position is shown in Fig. 5. There are no significant differences (larger than 2 e.s.d.'s) between the geometries of the two molecules.

The structure of the new molecule **3** consists of the phthalocyaninatoiron moiety with the two *trans*-complexed benzylamine ligands. The local coordination geometry can be considered as distorted octahedral. The observed six Fe–N bond lengths can be divided into two groups. The four somewhat shorter distances are associated with the phthalocyanine ring: Fe–N(1) 1.95(1) Å, Fe–N(3) 1.89(1) Å, Fe–N(5) 1.924(9) Å, and Fe–N(7) 1.90(1) Å<sup>2</sup>. These values are consistent with those reported in the literature for related complexes [6]. The two slightly longer Fe–N distances, Fe–N(9) 2.04(1) Å and Fe–N(10) 2.024(9) Å, arise from the benzylamine ligands. The bond angles about the octahedral Fe-center are rather normal, with the strongest deviation found in the *trans* relation of the two benzylamine ligands. This N(10)–Fe–N(9) angle at 173.9(4)° is slightly smaller than expected. The two remaining *trans* angles

<sup>1</sup>) Supplementary material can be obtained from the authors (P. S. P.).

<sup>2</sup>) Arbitrary atom numbering; for the systematic name, see *Exper. Part*.

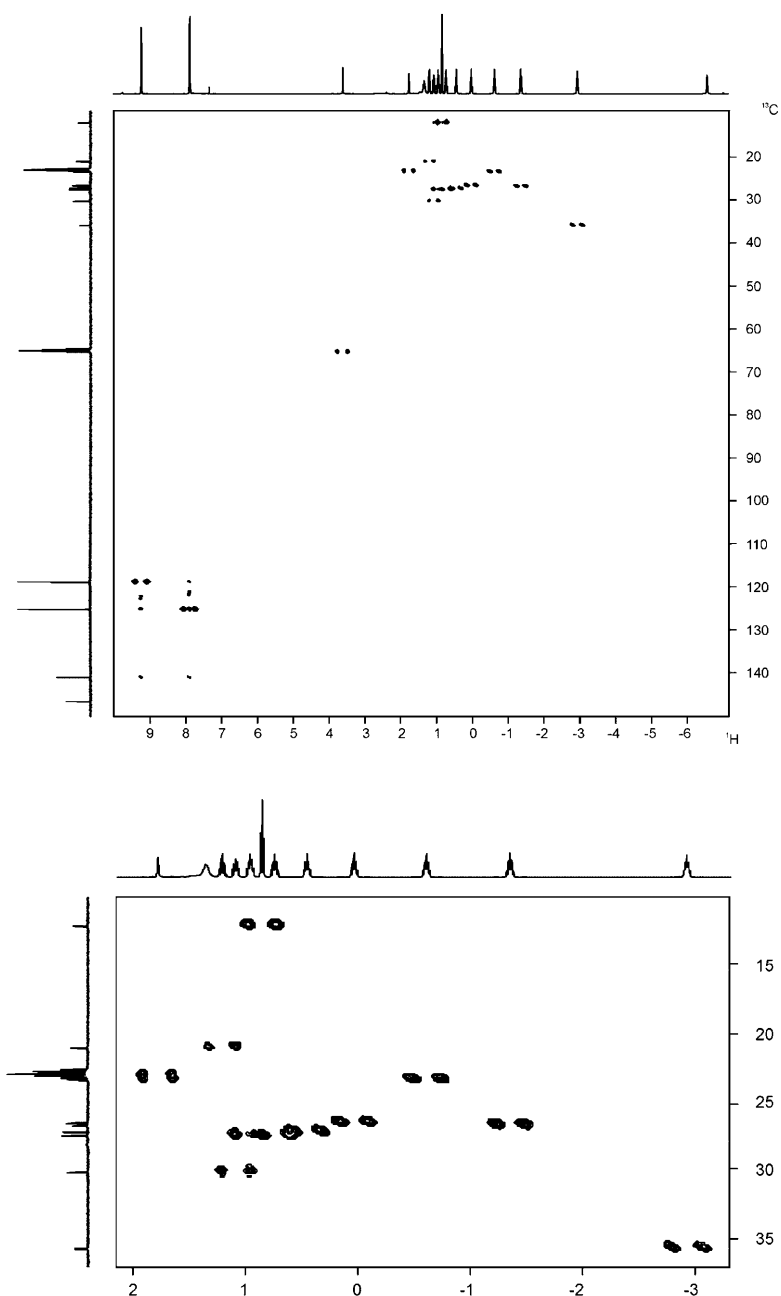


Fig. 3.  $^1\text{H}$ ,  $^{13}\text{C}$ -gHMOC Spectrum (500.23 MHz, 298 K,  $(\text{D}_8)$ THF) of  $[\text{Fe}(\text{decane-1-amine})_2(\text{pc})]$  **2**. Bottom: expansion of the aliphatic region. Top: in the high-frequency region, long-range correlations to the benzo C-atoms are observed, but not to the C-atoms in the imino position.

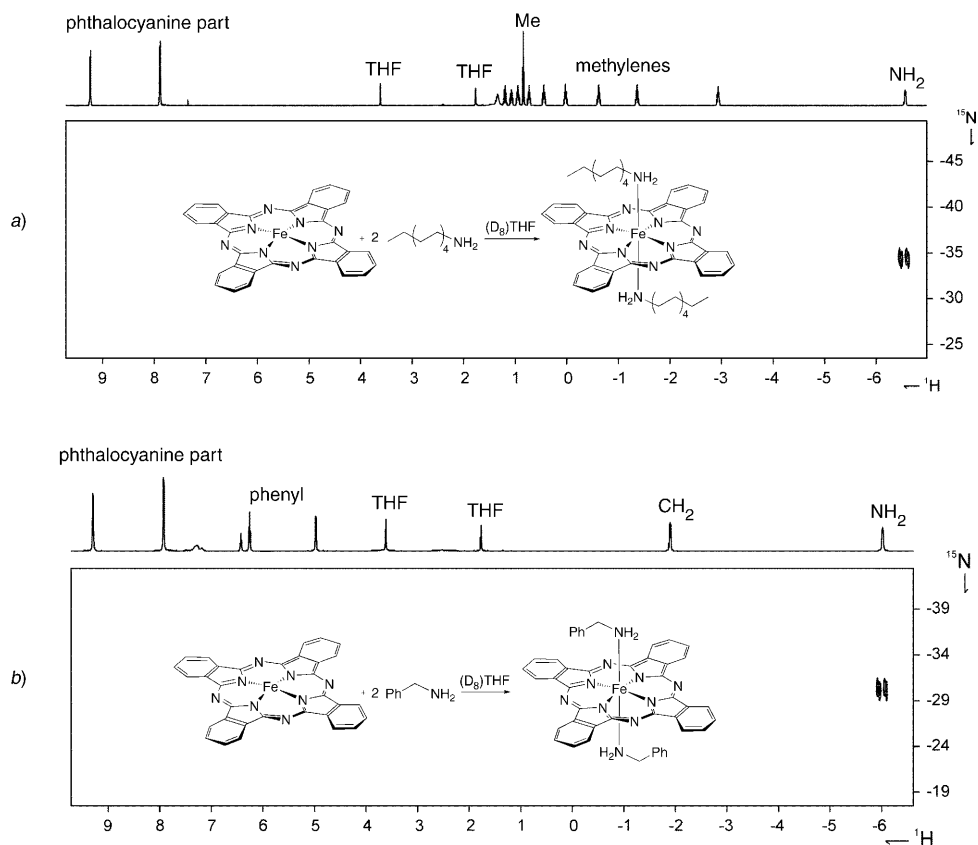


Fig. 4.  $^1\text{H},^{15}\text{N}$ -HMQC-NMR Spectrum (500.23 MHz, 298 K,  $(\text{D}_8)$ THF) of a)  $[\text{Fe}(\text{decylamine})_2(\text{pc})]$  **2** ( $\delta -34.8$ ,  $^1J(^{15}\text{N},^1\text{H})=66.4$ ) and b)  $[\text{Fe}(\text{benzylamine})_2(\text{pc})]$  **3** ( $\delta -30.5$ ,  $^1J(^{15}\text{N},^1\text{H})=68.0$  Hz)

are both close to  $180^\circ$ ,  $\text{N}(3)\text{--Fe--N}(7)^\circ$   $179.8(5)$ , and  $\text{N}(5)\text{--Fe--N}(1)$   $179.5(4)^\circ$ , and suggest a fairly regular arrangement of the phthalocyaninato system. The complexed phthalocyanine ring appears relatively flat.

**NMR Measurements of the CO Complex 4.** Scheme 2 shows that the reaction of a solution of **2** in  $(\text{D}_8)$ THF in an NMR tube with 3 bar of CO results in a mixture of a new CO complex **4**, free amine, and unreacted **2** (Fig. 6). Apart from a series of new signals in the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **4**, the  $^{13}\text{C}$ -NMR spectrum in the high-frequency (CO) region (Fig. 7) reveals a new signal at  $\delta$  198.3, which we assign to a complexed CO moiety. While the conversion to **4** is not complete, one can estimate from Fig. 6 that *ca.* 50% of the bis(amine) complex is converted to the monoamine CO complex, based on the 2 : 1 ratio of integrals found in the aliphatic region of the spectrum.

Monocarbonyl complexes of phthalocyaninatoiron(II),  $[\text{Fe}(\text{CO})\text{L}(\text{pc})]$ , L = various O-, S-, and N-donors, have been prepared [11] and characterized only by elemental analysis and IR data. No NMR data are provided for these molecules.

**Diffusion Data.** We have recently used pulsed gradient spin-echo (PGSE) NMR diffusion data to estimate molecular volumes in transition-metal complexes [12][13].

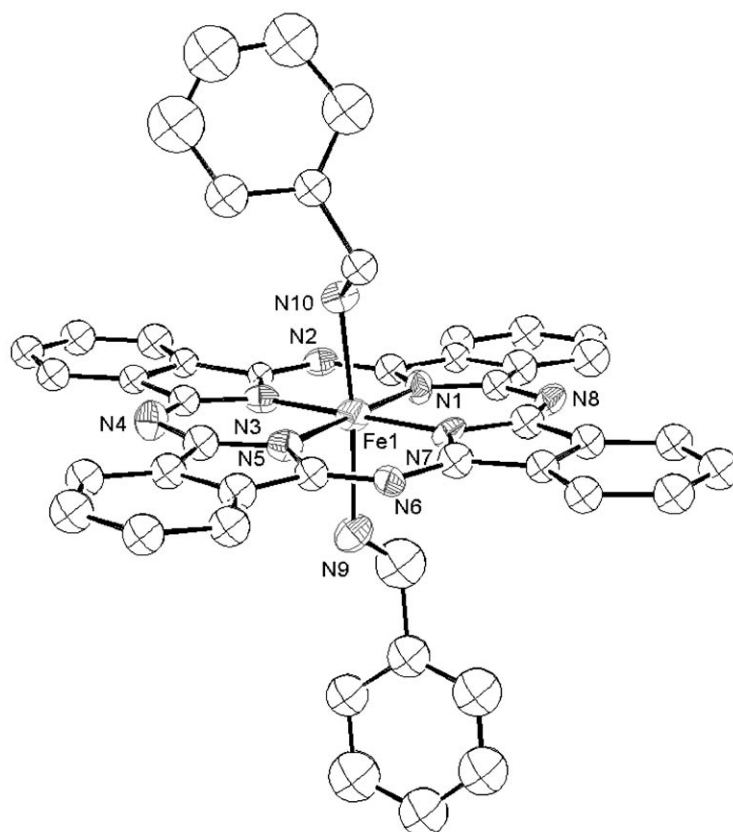
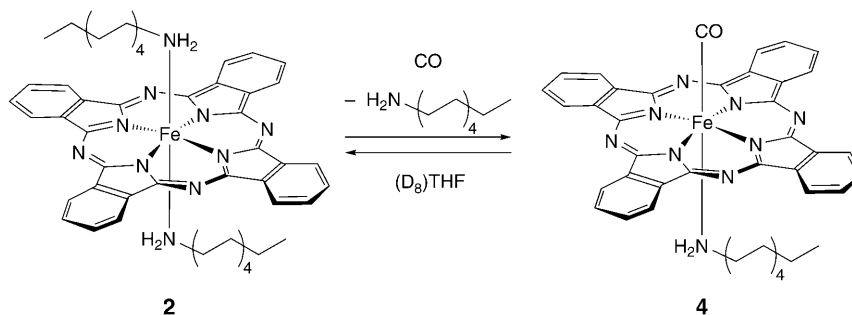


Fig. 5. ORTEP View of **3**. The THF molecules in the crystal are omitted for clarity. Arbitrary atom numbering<sup>2)</sup>.

Scheme 2



Given the possibility of some aggregation of the phthalocyanine moiety, we decided to estimate the solution volumes of both **2** and **3** via their  $^1\text{H}$  diffusion data and show these NMR results in *Table 1*. The values for the hydrodynamic radii  $r_{\text{H}}$  of 8.3 and 7.4 Å,

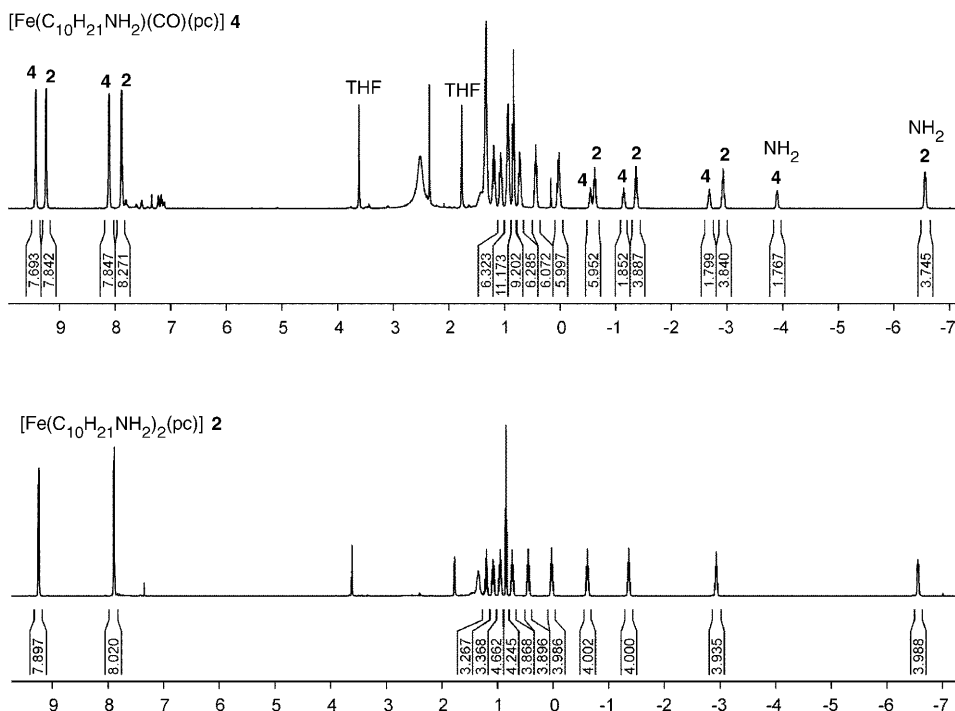


Fig. 6. <sup>1</sup>H-NMR Spectrum (500.23 MHz, 298 K, (D<sub>8</sub>)THF) of the mixture of [Fe(decan-1-amine)<sub>2</sub>(pc)] **2** and [Fe(CO)(decan-1-amine)(pc)] **4** (top), prepared by treating an NMR sample of **2** in the NMR tube with CO (3 bar). The spectrum of pure **2** (bottom) is also shown.

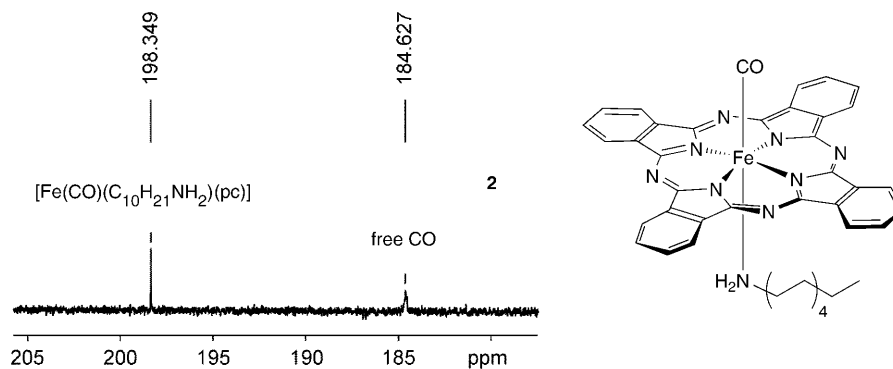


Fig. 7. Expansion of the CO region of the <sup>13</sup>C-NMR spectrum (125.79 MHz, 298 K, (D<sub>8</sub>)THF) of the mixture containing [Fe(decan-1-amine)<sub>2</sub>(pc)] **2** and [Fe(CO)(decan-1-amine)(pc)] **4**

respectively, are derived from Eqn. 1, the Stokes–Einstein relation. Therein,  $D$  is the measured diffusion constant,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $\eta$  the solvent viscosity, and  $r_H$  the hydrodynamic radius. The calculated  $r_H$  value of



7.4 Å for **3** is in excellent agreement with the value of *ca.* 7.4 Å based on our X-ray data, so that it is clear that, under our conditions, there is no significant aggregation [14].

Table 1.  $D$  [ $\times 10^{10} \text{ m}^2 \text{ s}^{-1}$ ] and  $r_H$  [Å] Values<sup>a)</sup> of Decan-1-amine, Benzylamine, and the Two Bis(amine)phthalocyaninatoiron(II) Complexes **2** and **3** in ( $D_8$ )THF at 299 K

	$D^a)$	$r_H^b)$
Decan-1-amine	16.0	3.0
Benzylamine	20.6	2.3
[Fe(decane-1-amine) <sub>2</sub> (pc)], <b>2</b>	5.70	8.3
[Fe(benzylamine) <sub>2</sub> (pc)], <b>3</b>	6.44	7.4

<sup>a)</sup> All at 60 mm. Experimental error  $\pm 2\%$ . <sup>b)</sup>  $\eta$  (THF, 299 K) =  $0.461 \cdot 10^{-3} \text{ Kg s}^{-1} \text{ m}^{-1}$ .

$$r_H = \frac{kT}{6\pi\eta D} \quad (1)$$

**3. Conclusions.** – As might be expected based upon known coordination-chemistry principles, the added ‘solubilizing’ amine reagent complexes the phthalocyaninatoiron derivative, thereby preventing [Fe(pc)] aggregation. The octahedral bis(amine) complexes formed are relatively stable in solution and can be readily characterized by both <sup>1</sup>H-NMR and X-ray methods. These 18-electron coordinatively saturated [Fe(pc)] complexes can lose an amine ligand, presumably *via* a dissociative mechanism, and (as suggested by the CO reaction with **2**) are sufficiently labile to allow a model gas molecule, in this case CO, to occupy the vacant coordination position. Although these results are not relevant with respect to nitrogen dioxide chemistry, they do provide a model for the molecular basis of the proposed sequence of events in the potential chemical sensors. Moreover, the new results confirm the previous interpretation based on optical spectroscopy and clearly show that the octahedral bis(amine) complex is stable and does not decompose up to 75°.

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### Experimental Part

*General.* All chemicals used for the sample preparation were obtained from Merck, Sigma-Aldrich, or Fluka, and were of reagent grade. The carbon monoxide was of research grade and was used as received. ( $D_8$ )THF was distilled over K/benzophenone prior to use. 1D- and 2D-NMR: Bruker-Avance-500 spectrometers; THF solns. at 299 K and 60 mm concentration;  $\delta$  in ppm rel. to SiMe<sub>4</sub>; unless otherwise stated, the NMR samples were prepared in standard 5-mm NMR tubes which were flushed with N<sub>2</sub>, oven-dried, and fitted with a Young-type cap.

*NMR Studies.* The sample temp. was calibrated before the PGSE measurements by introducing a thermocouple inside the bore of the magnet. The <sup>1</sup>H,<sup>15</sup>N-HMQC measurements were carried out by using a mixing time of 6 ms with 16–32 scans for each of the 512- $t_1$  increments recorded. The delay between increments was set to 0.5 s.

Diffusion measurements were performed by using the stimulated echo pulse sequence on a 400-MHz *Bruker-Avance* spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe with an actively shielded *Z*-gradient coil. The shape of the gradient pulse was rectangular, and its strength varied automatically in the course of the experiments. The measurements were carried out without spinning. The calibration of the gradients was carried out *via* a diffusion measurement of HDO in D<sub>2</sub>O, which afforded a slope of  $2.022 \cdot 10^{-4}$ . We estimate the experimental error in the *D* values to be  $\pm 2\%$ . All of the data leading to the reported *D* values afforded lines whose correlation coefficients were  $> 0.999$ , and 8–12 points were used for regression analysis. To check reproducibility, three different measurements with different diffusion parameters ( $\delta$  and/or  $\Delta$ ) were always carried out. The gradient strength was incremented in 8% steps from 10 to 98%. A measurement of <sup>1</sup>H and *T*<sub>1</sub> was carried out before each diffusion experiment, and the recovery delay was set to 5 times *T*<sub>1</sub>. In the diffusion experiments,  $\delta$  was set to 1.75 or 2 ms, and the number of scans were 16 per increment with a recovery delay of 10–60 s. Typical experimental times were 4–6 h.

*Crystal Structure.* X-Ray diffraction data for **3** · (3 THF) were collected at 120 K on a *Bruker-SMART-CCD* diffractometer. Crystallographic data are listed in Table 2. It proved impossible to obtain crystals of good quality. Crystals were poorly diffracting to a maximum  $2\theta < 40^\circ$ . This fact explains the limited number of observed reflections and the relatively high agreement factors. The collected intensities were corrected for *Lorentz* and polarization factors [15] and empirically for absorption using the *SADABS* program [16].

The structure was solved by direct and *Fourier* methods and refined by full-matrix least squares [17] (on *F*<sup>2</sup>). Due to the limited number of observed reflections, only the Fe- and N-atoms were refined anisotropically. The difference *Fourier* maps showed clearly the presence of three clathrated THF molecules that were refined isotropically. Upon convergence, the final *Fourier* difference map showed no sig-

Table 2. *Crystallographic Data for the Complex 3* · (3 THF)

Empirical formula	C <sub>81</sub> H <sub>63</sub> Fe <sub>1.5</sub> N <sub>15</sub> O <sub>3</sub>
<i>M</i> <sub>r</sub>	1378.24
<i>T</i> [K]	120(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	11.346(4)
<i>b</i> [Å]	15.426(5)
<i>c</i> [Å]	20.293(7)
$\alpha$ [°]	72.327(6)
$\beta$ [°]	81.587(5)
$\gamma$ [°]	81.860(6)
<i>V</i> [Å <sup>3</sup> ]	3330(2)
<i>Z</i>	2
$\rho_{\text{cal}}$ [g cm <sup>-3</sup> ]	1.375
$\mu$ [cm <sup>-1</sup> ]	3.96
$\lambda$ [Å] (MoK $\alpha$ )	0.71073
$\theta$ max [°]	19.95
Reflections measured	15739
Independent reflections	6147
Observed reflections [ $ F_o ^2 > 2.0\sigma( F^2 )$ ]	2627
Parameters	488
<i>R</i> <sub>int</sub>	0.1624
<i>R</i> (obs. refl.)	0.0708
<i>R</i> <sub>w</sub> <sup>2</sup> (obs. refl.)	0.1603
g.o.f.	0.951

$$R = \Sigma(|F_o - (1/k)F_c|) / \Sigma|F_o|, R_w^2 = [\Sigma w(F_o^2 - (1/k)F_c^2)^2 / \Sigma w|F_o^2|^2], \text{ g.o.f.} = [\Sigma_w(F_o^2 - (1/k)F_c^2)^2 / (n_o - n_v)]^{1/2}.$$

nificant peaks. The contribution of the H-atoms, in their calculated position, was included in the refinement by using a riding model. All calculations were carried out with the PC version of the programs WINGX [18], SHELX-97 [17], and ORTEP [19].

CCDC-290042 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) from the *Cambridge Crystallographic Data Centre*.

*Preparation of the [Fe(amine)<sub>2</sub>(pc)] Complexes 2 and 3 in-situ.* Into an oven-dried 5-mm NMR tube containing the [Fe<sup>II</sup>(pc)] salt (17 mg, 0.0299 mmol), (D<sub>8</sub>)THF (0.5 ml) and the corresponding amine [for **2**, decan-1-amine (12 µl, 0.0598 mmol); for **3**, benzylamine (7 µl, 0.0598 mmol)] was added. After a few minutes, the color of the solns. turned deep green.

*Bis(decane-1-amine)[29H,31H-phthalocyaninato(2-)-κN<sup>29</sup>,κN<sup>30</sup>,κN<sup>31</sup>,κN<sup>32</sup>]iron* ([Fe(decane-1-amine)<sub>2</sub>(pc)]; **2**). <sup>1</sup>H-NMR: -6.52 (4 H, NH<sub>2</sub>); -2.93 (4 H); -1.36 (4 H); -0.62 (4 H); -0.02 (4 H); 0.44 (4 H); 0.73 (4 H); 0.84 (6 H); 0.93 (4 H); 1.07 (4 H); 1.20 (4 H); 7.89 (8 H); 9.25 (8 H). <sup>13</sup>C-NMR (125.79 MHz): 11.9 (Me); 21.0 (CH<sub>2</sub>); 23.3 (CH<sub>2</sub>); 26.5 (CH<sub>2</sub>); 26.7 (CH<sub>2</sub>); 27.2 (CH<sub>2</sub>); 27.4 (CH<sub>2</sub>); 27.5 (CH<sub>2</sub>); 30.2 (CH<sub>2</sub>); 35.8 (CH<sub>2</sub>); 118.9 (CH, pc); 125.2 (CH, pc); 141.1 (C<sub>ipso</sub>, pc); 146.7 (C<sub>ipso</sub>, pc). Anal. calc. for C<sub>52</sub>H<sub>62</sub>ClFeN<sub>10</sub> (+ 1 pentane): C 71.68, H 7.81, N 14.67; found: C 70.93, H 7.62, N 14.73.

*Bis(benzenemethanamine)[29H,31H-phthalocyaninato(2-)-κN<sup>29</sup>,κN<sup>30</sup>,κN<sup>31</sup>,κN<sup>32</sup>]iron* ([Fe(benzylamine)<sub>2</sub>(pc)]; **3**). <sup>1</sup>H-NMR: -6.01 (4 H, NH<sub>2</sub>); -1.89 (4 H); 4.97 (4 H, Ph); 6.25 (4 H, Ph); 6.42 (2 H, Ph); 7.92 (8 H); 9.28 (8 H). <sup>13</sup>C-NMR (125.79 MHz): 39.6 (CH<sub>2</sub>); 118.5 (CH, pc); 123.6 (CH, pc); 123.9 (CH, Ph); 124.8 (CH, Ph); 124.9 (CH, Ph); 135.1 (C<sub>ipso</sub>, Ph); 140.7 (C<sub>ipso</sub>, Ph); 146.5 (C<sub>ipso</sub>, pc). Anal. calc. for C<sub>46</sub>H<sub>34</sub>ClFeN<sub>10</sub>: C 70.59, H 4.38, N 17.90; found: C 71.08, H 4.82, N 16.95.

*CO Chemistry.* A soln. of **2** in (D<sub>8</sub>)THF was prepared *in situ* as reported above and placed in a 5-mm NMR tube equipped with a *Young* valve. The NMR tube was then connected to the CO cylinder and pressurized to 3 bar of CO. The valve was closed, and the NMR tube was detached from the cylinder. The tube was shaken and immediately transferred into the NMR probe. The reaction to *carbonyl(decane-1-amine)[29H,31H-phthalocyaninato(2-)-κN<sup>29</sup>,κN<sup>30</sup>,κN<sup>31</sup>,κN<sup>32</sup>]iron* ([Fe(CO)(C<sub>10</sub>H<sub>21</sub>NH<sub>2</sub>)(pc)]; **4**) was followed by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy at r.t.

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