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High-Valent Iron Phthalocyanine μ-Nitrido Dimers

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Since we first described the (μ-oxo)iron(III) dimer $(PcFe)_2O$,[1] isolated in two different crystalline isomers, i.e. μ-oxo(**1**) (**1a**) and μ-oxo(**2**) (**2a**),[2,3] the number of iron phthalocyanine complexes having the metal atom in an oxidation state higher than 2 has been extended with the synthesis and characterization of several dimeric and monomeric iron(III)-containing derivatives.[4] Accessibility to even higher oxidation states was established with the synthesis and characterization of the μ-nitrido complex $(PcFe)_2N$ (**3**),[5] formally a mixed valence iron(III)–iron(IV) dimer, which, however, should be more correctly formulated as having two equivalent iron centers with oxidation states intermediate between III and IV, as was indicated by EPR and spectroelectrochemical work in pyridine solution.[5] These solution studies[5] also confirmed that the species $[((py)PcFe)_2N]^+$ (**8**), previously reported as a PF_6^- salt,[5a] can be obtained as a stable solid by a one-electron oxidation of **3**. We report here further information on the μ-nitrido complex **3**, and present a new series of iron(IV) μ-nitrido dimers of formulas $((PcFe)_2N)(PF_6)$ (**5**) and $[((L)PcFe)_2N](PF_6)$ (L = 4-Mepy (**7**), py (**8**), pip (**9**), and 1-Meim (**10**)). These complexes are of interest, in relation to the presence and role of iron(IV) in heme- or heme-like-containing systems. Identification and characterization of the species **5** and **7–10** was achieved by elemental and thermogravimetric analysis, IR, Mössbauer and EPR spectra, and magnetic susceptibility measurements. Perhaps, species similar to **7–10** can be obtained for the monopositively charged porphyrin species $[((TPP)Fe)_2N]^+$ (**6**), prepared by a one-electron oxidation of $((TPP)Fe_2N$ (**4**), as might be determined by the increased Lewis acidity at the Fe atoms of **4** (unable to give solid stable N-base adducts) when converted into **6**, as indeed occurrs for species **3** (unreactive towards N-bases) and **5** (reactive).

Results and Discussion

Table I summarizes the Mössbauer data obtained at 77 K on the μ-nitrido species under discussion (**3**, **5**, and **7–10**), together with data for the μ-oxo dimers **1a** and **2a** and the similar tetraphenylporphyrin μ-nitrido species $((TPP)Fe)_2N$ (**4**) and $[((TPP)Fe)_2N]^+$ (**6**).[6] Complex **3** shows a single doublet indicative of the presence of one iron site, with an isomer shift of 0.06 mm/s. This value, significantly lower than those found for the μ-oxo iron(III) species **1a** and **2a**, suggests a decreased s electron density at the iron nucleus and, hence, a higher oxidation state. Also, the isomer shift is roughly intermediate between those observed for the μ-oxo dimers **1a** and **2a**, which contain only iron(III), and the series of the N-base adducts **7–10**, which contain only iron(IV) (see Table I and discussion below). Thus, the Mössbauer data for complex **3**, in keeping with our previous results,[5] strongly support the presence of equivalent iron sites within this dimer, an averaged intermediate oxidation state between III and IV for the Fe ions on the Mössbauer time scale, and the symmetrical representation, $PcFe^{III\,1/2}$–N–$Fe^{III\,1/2}Pc$, as the most plausible description for the charge distribution on the dimer. The isomer shift for **3** is definitely lower than that observed for the tetraphenylporphyrin analogue $((TPP)Fe)_2N$ (**4**) (Table I), even when the different temperatures of the measurements are considered. No simple explanation can be given either for the observed difference in the isomer shifts or for the large difference in the quadrupole splitting values (Table I), at the present stage of information. The room-temperature magnetic moment for **3** is 2.13 μ_B per molecule, consistent with the presence of one unpaired electron per dimer, as might be expected.[8]

Table I

complex[a]	*T*, K	δ,[b] mm/s	ΔE_q, mm/s	Λ,[c] mm/s	ref
$(PcFe)_2O$ (**1a**) (μ-oxo(**1**))	77	0.36	0.44	0.16	7, 4a
$(PcFe)_2O$ (**2a**) (μ-oxo(**2**))	77	0.26	1.26	0.14	4a
$(PcFe)_2N$ (**3**)	77	0.06	1.76	0.19	*d*
$((TPP)Fe)_2N$ (**4**)	131	0.18	1.08		6
$((PcFe)_2N)(PF_6)$ (**5**)	77	−0.10	2.06	0.16	*d*
$(((TPP)Fe)_2N)(ClO_4)$ (**6**)	131	0.03	2.00		6
$[((4\text{-}Mepy)PcFe)_2N](PF_6)$ (**7**)	77	−0.10	1.76	0.17	*d*
$[((py)PcFe)_2N](PF_6)$ (**8**)	77	−0.09	1.76	0.20	*d*
$[((pip)PcFe)_2N](PF_6)$ (**9**)	77	−0.09	1.73	0.16	*d*
$[((1\text{-}Meim)PcFe)_2N](PF_6)$ (**10**)	77	−0.09	1.52	0.13	*d*

[a] Impurities (<5%), not detailed here, were present, as well evidenced by the computer fitting, in the Moessbauer spectra, of samples of the N-base adducts **7**, **9**, and **10**. [b] Referred to Fe metal. [c] Half-width at half-maximum height. [d] This work.

A metal-centered one-electron oxidation takes place when **3** is oxidized by the ferrocenium cation to complex **5**, as is indicated by the single doublet observed in the Mössbauer spectrum of **5**. This implies the presence of equivalent iron sites within this dimer; also, the negative value of the isomer shift (−0.10 mm/s) clearly

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(1) Ercolani, C.; Monacelli, F.; Rossi, G. *Inorg. Chim. Acta* **1980**, *44*, L215–L216. Abbreviations used in the present paper: Pc = phthalocyaninato dianion, TPP = tetraphenylporphyrinato dianion, 4-Mepy = 4-methylpyridine, py = pyridine, pip = piperidine, 1-Meim = 1-methylimidazole.

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(4) (a) Ercolani, C.; Gardini, M.; Murray, K. S.; Pennesi, G.; Rossi, G.; Zwack, P. R. *Inorg. Chem.* **1987**, *26*, 3539–3543. (b) Kalz, W.; Homborg, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 470–483. (c) Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W. *Inorg. Chem.* **1986**, *25*, 2539–2545 and references therein.

(5) (a) Goedken, V. L.; Ercolani, C. *J. Chem. Soc., Chem. Commun.* **1984**, 378–379. (b) Bottomley, L. A.; Gorce, J.-Noel; Goedken, V. L.; Ercolani, C. *Inorg. Chem.* **1985**, *24*, 3733–3737.

(6) English, R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1983**, *22*, 368–370.

(7) Kennedy, B. J.; Murray, K. S.; Zwack, P. R.; Homborg, H.; Kalz, W. *Inorg. Chem.* **1985**, *24*, 3302–3305.

(8) While this manuscript was in preparation, Dr. K. S. Murray kindly sent to us a manuscript (*Inorg. Chim. Acta*, in press) on some oxidized μ-nitrido)iron phthalocyanine complexes different from those reported here. As to the starting material, i.e. $(PcFe)_2N$, described as obtained by a different route, our results (Mössbauer data, room-temperature magnetic moment, etc.) appear to be practically coincidental with those reported by Murray et al., with only a small difference in the room-temperature magnetic moment. We are very grateful to Dr. Murray for making his paper available to us prior to publication.

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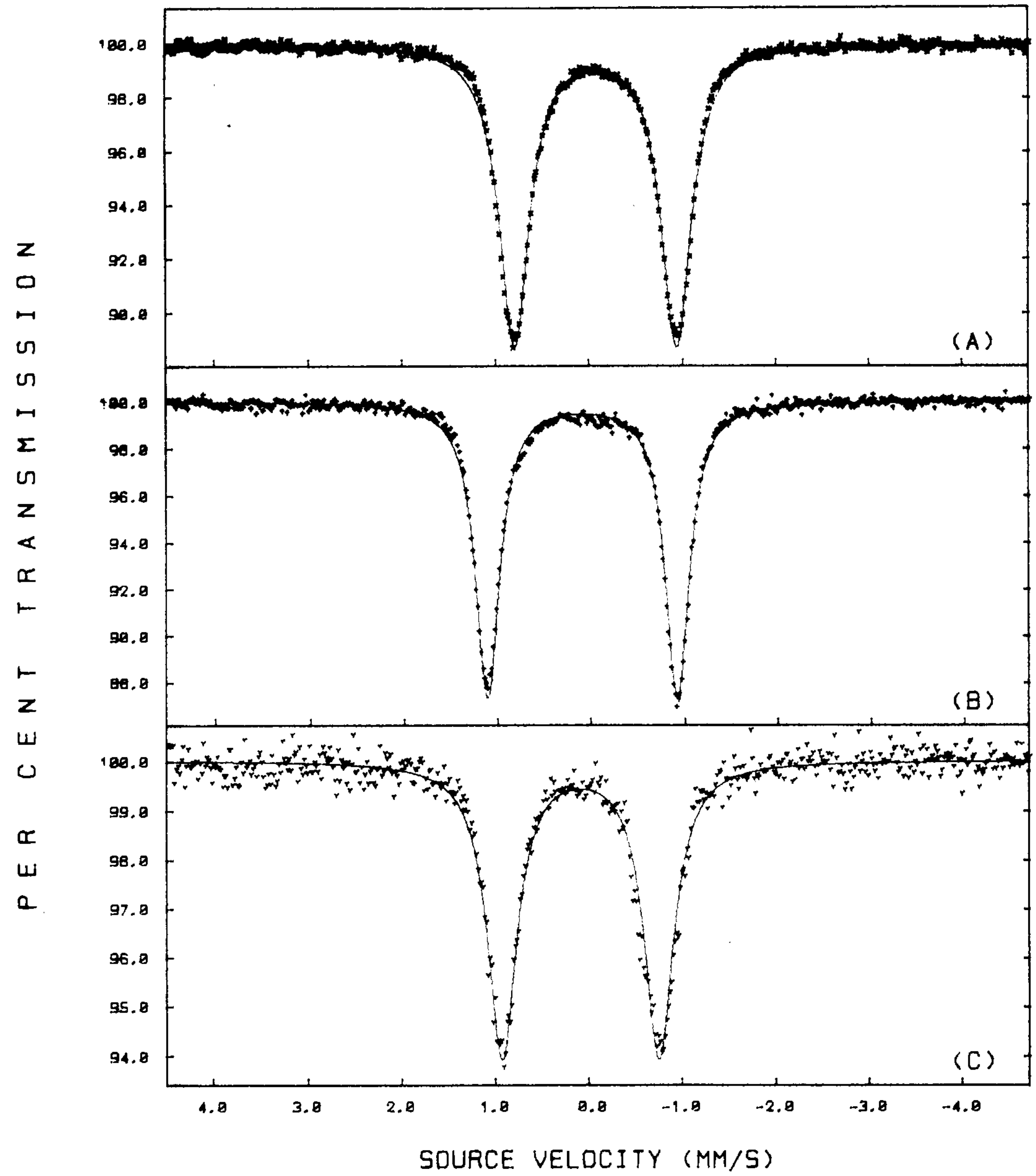

Figure 1. Mössbauer spectra of $(PcFe)_2N$ (A), $[(PcFe)_2N](PF_6)$ (B), and $[((py)PcFe)_2N](PF_6)$ (C).

corresponds to iron(IV).[6] There is a regular variation of both the isomer shift and the quadrupole splitting values in going from **1** and **2** (iron (III)), through **3** (iron(III$^1/_2$)), to **5** (iron(IV)). It is interesting that **5**, and its corresponding iron(IV)–TPP analogue **6** (Table I) show quite similar isomer shifts and quadrupole splitting. However, although similar, the isomer shift for **5** is definitely lower than that of **6**, consistent with the results for **3** and **4**. Elemental and thermogravimetric analyses, as well as IR spectra for **5**, suggest the presence of water and acetone, roughly corresponding to the formula $[(PcFe)_2N](PF_6)\cdot(H_2O)_2\cdot$acetone. Presently we are unable to definitely establish whether these additional solvent molecules are interstitial or are coordinated at the external axial sites in the dimer **5**.

The μ-nitrido-bridged dimers **7–10** parallel the homogeneous series of six-coordinate μ-oxo–iron(III) N-base adducts of formula $((L)PcFe)_2O$ (L = 4-Mepy, py, pip, 1-Meim).[4a] These μ-oxo species give quadrupole doublet Mössbauer spectra with isomer shifts and quadrupole splittings in the ranges 0.17–0.20 mm/s and 1.55–1.75 mm/s, respectively, indicative of equivalent low-spin iron(III) sites.[4a,c] In the Mössbauer spectra of the μ-nitrido species **7–10**, only one quadrupole doublet is observed with a isomer shift of −0.10 mm/s and a quadrupole splitting in the range 1.52–1.76 mm/s. The isomer shift values are definitely lower, as expected, than those found in the series of (μ-oxo)iron(III) complexes and for the precursor, **3** (iron(III 1/2)), and fall in the range expected for iron(IV) as is the case of **5**. Thus, conversion of **5** into its corresponding six-coordinate N-base adducts leaves the positive charge entirely located on the two Fe ions of these bimetallic systems.

IR and EPR spectral measurements indicate a metal-centered oxidation when **3** is oxidized by the ferrocenium cation to **5**. They also confirm that **5** is converted into species **7–10** without any shift of the positive charge from the iron centers to the phthalocyanine ligands. Oxidation of **3** to **5** causes complete disappearance of the very strong ν_{as}(Fe-N-Fe) observed for **3** at 915 cm^{-1}[5] (Figure 2A,B). A residual sharp peak located at 910 cm^{-1} for **5**, commonly present at that frequency for phthalocyanine complexes, is assigned to a skeletal vibration of the phthalocyanine chromophore. ν_{as}(Fe-N-Fe) is also absent in the IR spectra of complexes **7–10** (see Figure 2C for the 4-Mepy adduct **7**). Intense absorptions at 845 (vs) and 558 cm^{-1} (s), due to PF_6^-, are observed in the IR spectra of **5** and **7–10**. the IR spectrum of **5** shows absorptions due to water (3600–3200 cm^{-1}, vvw) and acetone (1690 cm^{-1}, s). Typical absorptions due to the N-bases appear in the spectra of the complexes **7–10**, which do not show bands due to water and acetone. Neither the IR spectrum of **5** nor those of **7–10** show the spectral features associated with the presence of the phthalocyanine radical cation ($Pc^{\bullet -}$).[9] The practically

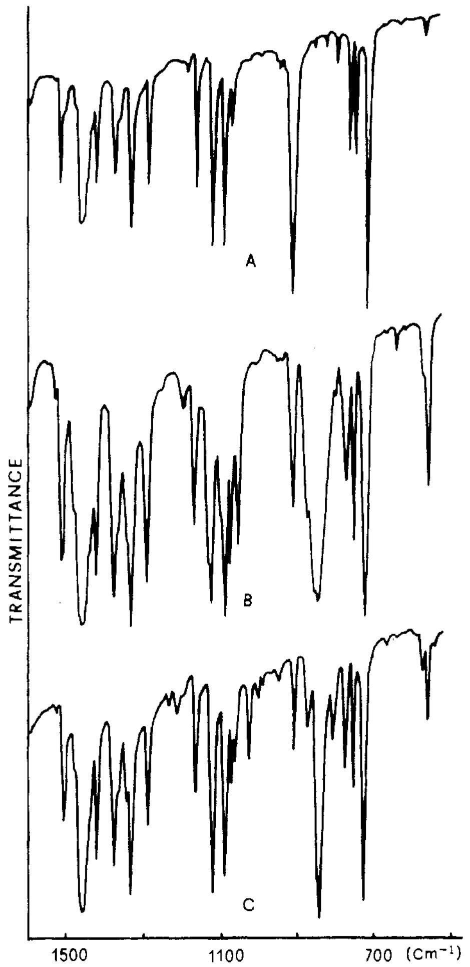

Figure 2. IR spectra of $(PcFe)_2N$ (A), $[(PcFe)_2N](PF_6)$ (B), and $[((py)PcFe)_2N](PF_6)$ (C).

complete disappearance of the signals present in the EPR spectrum of **3** ($g_{\parallel} = 2.03$, $g_{\perp} = 2.13$)[5] results from the oxidation to **5**, which is EPR silent, with the absence of even a trace of absorption at $g = 2$, as might be found for the formation of a phthalocyanine radical. A similar situation is found for the EPR spectra of **7–10**, indicating that there has been no substantial rearrangement of the charge distribution between the Fe–N–Fe moiety and the phthalocyanine ligands as a result of the ligation of the N-bases. In-plane location and six coordination for the Fe atoms in the N-base adducts **7–10** reiterate the closely resembling situation proposed for the corresponding μ-oxo adducts[4a] and very recently definitely established by X-ray work for the 1-Meim adduct, i.e. $((1\text{-Meim})PcFe)_2O$.[10] Species **7–10** appear to be unprecedented in the literature as solid, stable six-coordinate iron species among the few known μ-nitrido dimers formed with macrocyclic porphyrinlike systems.

Experimental Section

$(Fc)PF_6$. This ferrocenium salt was prepared by suspending ferrocene (10 g) for 5–6 h in a diluted aqueous solution of hydrochloric acid and hydrogen peroxide. The intensively blue solution obtained is then separated by the solid unreacted ferrocene by filtration, and an excess of ammonium hexafluorophosfate is added to it. The solid bluish $(Fc)PF_6$ formed is filtered, washed with methyl alcohol, and dried under vacuum (10^{-2} mmHg) (2.5 g). Anal. Calcd for $C_{10}H_{10}F_6FeP$: C, 36.5; H, 3.02. Found: C, 36.18; H, 3.02.

$(PcFe)_2N$ (3). Analytically pure samples of **3**, prepared by the method previously reported,[5] generally show room-temperature magnetic moments higher than 2.5–2.6 μ_B. Elimination of small amounts of paramagnetic impurities present in these samples can be obtained by oxidation of **3** to **5**, followed by the reverse process performed in the presence of piperidine and water (see below), with eventual duplication of the procedure. Reproducible, room-temperature magnetic moments of 2.13 ± 0.05 μ_B are obtained for the purified samples.

$((PcFe)_2N)PF_6$ (5). This complex can be obtained by suspending **3** (600 mg, 0.52 mmol) in a solution of $(Fc)PF_6$ (380 mg, 1.19 mmol) in acetone (200 mL) and stirring the reaction mixture at room temperature for 24 h. Solid crystalline **5** is separated by filtration from the solution, washed with acetone, and dried under vacuum (10^{-2} mmHg). The complex systematically shows the presence of water and acetone. It roughly analyzes for the formula $((PcFe)_2N)PF_6\cdot 2H_2O\cdot$acetone: Anal. Calcd for $C_{67}H_{42}N_{17}F_6Fe_2O_3P$: C, 57.90; H, 3.05; N, 17.13; Fe, 8.03. Found: C, 56.97; H, 3.27; N, 15.86; Fe, 8.33.

$[((4\text{-Mepy})PcFe)_2N]PF_6$ (7). This complex can be obtained by dissolving **5** (240 mg) in 4-Mepy (25 mL). The solution is kept for 30 min at room temperature. After filtration, ether is added to the solution to precipitate the complex. The solid formed is separated from the solution by filtration, washed with ether, and dried under vacuum (10^{-2} mmHg) (190 mg). Anal. Calcd for $C_{76}H_{46}F_6Fe_2N_{19}P$: C, 61.60; H, 3.13; N, 17.95. Found: C, 61.71; H, 3.36; N, 17.38.

$[((py)PcFe)_2N]PF_6$ (8). This adduct can be prepared as previously described.[5b] It can also be obtained by repeating twice the following procedure: **5** (270 mg) is dissolved in pyridine (15 mL) and the solution obtained is kept at room temperature for 30 min. After filtration, water is added to the solution to precipitate the complex, which is then separated, washed with water and 95% ethanol, and dried under vacuum (10^{-2} mmHg) (150 mg). Anal. Calcd for the formula $C_{74}H_{42}F_6Fe_2N_{19}P$: C, 61.14; H, 2.91; N, 18.30. Found: C, 61.34; H, 2.94; N, 18.0.

$[((pip)PcFe)_2N]PF_6$ (9). **5** (120 mg) is suspended in a mixture of ether (3–4 mL) and piperidine (0.7 mL) and the suspension stirred at room temperature for 2 h. After filtration, the solid material is washed with ether and dried under vacuum (10^{-2} mmHg). Anal. Calcd for the formula $C_{74}H_{54}F_6Fe_2N_{19}P$: C, 60.63; H, 3.71; N, 18.15. Found: C, 59.75; H, 3.59; N, 17.61. Addition of water to a solution of **5** in pure piperidine kept at room temperature for 30–40 min determines the formation of a precipitate that is identified as the μ-nitrido species **3**. Reiteration of the conversion of **3** into **5**, and reduction of the latter in pure piperidine, has allowed the purification of **3**, as indicated above for this complex.

$[((1\text{-Meim})PcFe)_2N]PF_6$ (10). A mixture obtained by suspending **5** (300 mg) in 1-Meim (15 mL) is kept under stirring at room temperature for 30-40 min. After filtration, ether is added to the solution and a precipitate is formed. The solid is separated from the solution by filtration, washed with ether, and dried under vacuum (10^{-2} mmHg). Anal. Calcd for the formula $C_{72}H_{44}F_6Fe_2N_{21}P$: C, 59.24; H, 3.04; N, 20.14. Found: C, 58.68; H, 3.32; N, 19.79.

Physical Measurements. IR spectra were recorded on a Perkin Elmer 983 spectrophotometer by using Nujol mulls and NaCl or CsI disks. EPR spectra were obtained on a Varian V 4502-4 spectrometer (X-band) at 110 K. Magnetic susceptibility measurements were obtained on a Gouy balance. Mössbauer spectra were obtained at 77 K on a conventional constant-acceleration spectrometer, which utilizes a room-temperature rhodium matrix cobalt-57 source. The spectra were fitted to Lorentzian line shapes by using a standard least-squares computer minimization technique.

Registry No. 3, 98395-07-4; **5**, 111348-97-1; **7**, 111378-76-8; **8**, 98395-09-6; **9**, 111378-78-0; **10**, 111378-80-4.

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(10) Rossi, G.; Goedken, V. L.; Ercolani, C.; Dzugan, S. J., unpublished results.

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Ligand Substitution in $(Ind)W(CO)_3Cl$ and $(Ind)W(CO)_3^-Na^+$ (Ind = Indenyl): Examples of Mixed Associative and Dissociative Substitution

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The greater reactivity of η^5-indenyl complexes of the transition elements when compared to their η^5-cyclopentadienyl analogues

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