*Inorg. Chem.* **2001,** *40,* 2963−2967

# Metal- and Ligand-Centered Monoelectronic Oxidation of $\mu$-Nitrido[((tetraphenylporphyrinato)manganese)(phthalocyaninatoiron)], [(TPP)Mn−N−FePc]. X-ray Crystal Structure of the Fe(IV)-Containing Species [(THF)(TPP)Mn−N−FePc($H_2O$)]($I_5$)·2THF

**Maria Pia Donzello,[†] Claudio Ercolani,*,[†] Umberto Russo,[‡] Angiola Chiesi-Villa,[§] and Corrado Rizzoli[§]**

Dipartimento di Chimica, Università degli Studi di Roma “La Sapienza”, I-00185 Roma, Italy,
Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova,
I-35131 Padova, Italy, and Dipartimento di Chimica Generale, Università di Parma, I-43100 Parma, Italy

*Received August 4, 2000*

The reaction of $\mu$-nitrido[((tetraphenylporphyrinato)manganese)(phthalocyaninatoiron)], [(TPP)Mn−N−FePc], with $I_2$ in THF develops with the formation of two different species, i.e., [(THF)(TPP)Mn−N−FePc($H_2O$)]($I_5$)·2THF (**I**) and [(TPP)$Mn^{IV}$−N−$Fe^{III}$Pc]($I_3$) (**II**). On the basis of single-crystal X-ray work and Mössbauer, EPR, Raman, and magnetic susceptibility data, **I**, found to be isostructural with the corresponding Fe−Fe complex, is shown to contain a low-spin triatomic $Mn^{IV}$═N═$Fe^{IV}$ system (metal-centered oxidation). Data at hand for **II** (Mössbauer, EPR, Raman) show, instead, that oxidation takes place at one of the two macrocycles, very likely TPP (ligand-centered oxidation). The same cationic fragment present in **I**, and containing the $Mn^{IV}$═N═$Fe^{IV}$ bond system**,** is also obtained when (TPP)Mn−N−FePc is allowed to react in THF with (phen)$SbCl_6$ (molar ratio 1:1). There are indications that the use of (phen)$SbCl_6$ in excess (2:1 molar ratio), in benzene, probably determines further oxidation with the formation of a species showing the combined presence of the $Mn^{IV}$−$Fe^{IV}$ couple and of a $\pi$-cation radical.

## Introduction

$\mu$-Nitridobis[(tetraphenylporphyrinatoiron)], [(TPP)Fe−N−Fe(TPP)], among the complexes of general formula (L)M−N−M(L) (L = a tetrapyrrolic macrocycle), is the first one and nearly the exclusive representative example, widely investigated,[1] of a porphyrinato derivative, which has its counterpart, PcFe−N−FePc,[2] in the field of the phthalocyanine complexes. Both species, formally mixed-valence Fe(III)−Fe(IV) entities, and, indeed, characterized by the presence of iron atoms sharing the same oxidation state between +3 and +4, i.e., Fe(+3.5), have allowed the synthesis, through monoelectronic oxidation, of several $\mu$-nitrido species containing Fe(IV)−Fe(IV) couples, i.e., high valent iron.[2,3] PcRu−N−RuPc has also been reported,[4] the only species known to involve a second row transition metal. The first and so far unique member reported of the class (L)M−N−M(L′) was the mixed-ligand Fe−Fe complex (TPP)Fe−N−FePc,[5,6] again, noteworthy, characterized by the presence of two Fe centers in an intermediate oxidation state (+3.5), and capable of undergoing monoelectronic oxidation with formation of an Fe(IV) containing species of formula [(THF)(TPP)$Fe^{IV}$−N−$Fe^{IV}$Pc($H_2O$)]($I_5$)·2THF, structurally elucidated by single-crystal X-ray work.[6] Among the species containing the $Fe^{IV}$−N−$Fe^{IV}$ fragment, two additional examples have been recently reported, i.e., $\{[(N_3)PcFe]_2N\}^{-}$ [7] and $\{[(TTP)Fe]_2N\}(SbCl_6)$.[8]

In a development of our investigation in the field of such type of $\mu$-nitrido complexes, we recently reported on the

---

[†] Università degli Studi di Roma “La Sapienza”. E-mail: claudio.ercolani@uniroma1.it.
[‡] Università di Padova.
[§] Università di Parma.

(1) (a) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747. (b) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623. (c) Kadish, K. M.; Bottomley, L. A.; Brace, J. G., Winograd, N. *J. Am. Chem. Soc.* **1980**, *102*, 4341. (d) Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 7982. (e) Tatsumi, K.; Hoffman, R.; Whangbo, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 509. (f) Tatsumi, K; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328. (g) Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *J. Am. Chem. Soc.* **1981**, *103*, 3195. (h) Bottomley, L. A.; Garrett, B. B. *J. Am. Chem. Soc.* **1982**, *104*, 1260. Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1983**, *103*, 1830. (i) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1983**, *22*, 368. (j) Bocian, D. F.; Findsen, E. W.; Hoffman, J. A., Jr.; Schick, G. A.; English, D. R., Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1984**, *23*, 800. (k) English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1985**, *24*, 122.

(2) (a) Goedken, V. L.; Ercolani, C. *Chem. Commun.* **1984**, 378. (b) Bottomley, L. A.; Gorce, J.-N.; Goedken, V. L.; Ercolani, C. *Inorg. Chem.* **1985**, *24*, 3733. (c) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G.; Russo, U. *Inorg. Chem.* **1988**, *27*, 422. (d) Kennedy, B. J.; Murray, K. S.; Homborg, H.; Kalz, W. *Inorg. Chim. Acta* **1987**, *134*, 19. (e) Bakshi, E. N.; Delfs, C. D.; Murray, K. S.; Peters, B.; Homborg, H. *Inorg. Chem.* **1988**, *27*, 4318.

(3) Ercolani, C.; Floris, B. *Phthalocyanines − Properties and Applications*; Leznoff C. C., Lever, A. B. P., Eds; VCH Publishers: New York, 1993; Vol. 2, pp 1−43; Vol. 4, 405−425. Abbreviations used in this paper: THF = tetrahydrofuran; Pc = phthalocyaninato anion; TPP = tetraphenylporphyrinato anion; TTP = tetratolylporphyrinato anion; OPTAP = octaphenyltetraazaporhyrinato anion; phen($SbCl_6$) = phenoxathiin hexachloroantimonate.

(4) Rossi, G.; Gardini, M.; Pennesi, G.; Ercolani, C.; Goedken, V. L. *J. Chem. Soc., Dalton Trans.*, **1989**, 193.

(5) Ercolani, C.; Hewage, S.; Heucher, R.; Rossi, G. *Inorg. Chem.* **1993**, *32*, 2975.

(6) Ercolani, C.; Jubb, J.; Pennesi, G.; Russo, U.; Trigiante, G. *Inorg. Chem.* **1995**, *34*, 2535.

(7) Kienast, A.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 233.

(8) Li, M.; Shang, M.; Ehlinger, N.; Schulz, C. E., Scheidt, W. R. *Inorg. Chem.* **2000**, *39*, 580.

10.1021/ic000874m CCC: $20.00

synthesis, characterization, and redox properties of a new $\mu$-nitrido dimer, [(TPP)Mn−N−FePc],[9] a rare example of a new class of formally mixed-valence (III, IV) complexes of formula (L)M−N−M′(L′), containing different macrocycles and metal centers. To our knowledge, the only other reported member of this class of $\mu$-nitrido species is [(TPP)Fe−N−RuPc],[6] which contains an Fe(IV)−Ru(III) couple, and undergoes a ligand-centered monoelectronic oxidation with formation of the [(TPP)-Fe$^{IV}$−N−Ru$^{III}$Pc]$^{\cdot+}$ cation radical moiety.[6] Instead, indications for [(TPP)Mn−N−FePc][9] were for a metal-centered one-electron abstraction with formation of a Mn(IV)−Fe(IV) couple; however, the process, operated in $HClO_4$ (10%) through an intriguing procedure, led to the formation of a material (later referred here as "perchlorate") containing three slightly different Fe(IV) species that could not be given a precise formulation.[9] Recently, a Mn−Fe $\mu$-nitrido species containing the octaphenyltetraazaporphyrinato anion, i.e., (OPTAP)Mn−N−Fe(OPTAP), belonging to the class (L)M−N−M′(L), has been reported,[10] although in the absence of detailed structural work.

It is shown here that monolectronic oxidation of [(TPP)Mn−N−FePc] can be cleanly carried out by using either $I_2$ (excess) or (phen)$SbCl_6$ (1:1 molar ratio). Oxidation by $I_2$ leads to the species [(THF)(TPP)Mn−N−FePc($H_2O$)]($I_5$)·2THF (**I**), and often, curiously, under apparently the same reaction conditions, also to the formation of a species formulated as [(TPP)Mn−N−FePc]($I_3$) (**II**). **I** represents the first example of a heteroleptic and heterobimetallic $\mu$-nitrido bridged species whose the structure has been solved by single-crystal X-ray work. Complexes **I** and **II**, and related species, are examined here on the basis of X-rays, IR, Raman, EPR, Mössbauer, and magnetic data. This work further extends the series of $\mu$-nitrido species containing Fe(IV) centers surrounded by tetrapyrrolic macrocycles.

## Experimental Section

**Chemicals.** Pure solvents (THF, pentane, heptane, ethanol, benzene) and reagents ($I_2$, $NaBH_4$, phenoxathiin, $SbCl_5$) were obtained from Carlo Erba or Fluka. THF and benzene were made anhydrous by refluxing them over potassium and were freshly distilled before use. Phen($SbCl_6$), was prepared following the procedure reported in the literature.[11] PcFe was purchased from Eastman. (TPP)$MnN_3$ was prepared as described elsewhere.[12] Recrystallization of (TPP)$MnN_3$ from $CHCl_3$/hexane leads occasionally to the formation of crystals which show an IR spectrum and elemental analyses not exactly corresponding to those expected for the formation of the simple unsolvated azide. Single-crystal examination of these crystals allowed the identification of a new solvated species having formula [(TPP)$MnN_3$]($CHCl_3$)$_{0.5}$.[13] Its structure is reported in the Supporting Information as complex S1.[14]

**[(TPP)Mn−N−FePc].** This species was obtained from (TPP)$MnN_3$ and (Pc)Fe as previously reported.[9]

**[(THF)(TPP)Mn−N−FePc($H_2O$)]($I_5$)·2THF (I) and [(TPP)Mn−N−FePc]($I_3$) (II).** [(TPP)Mn−N−FePc] (191 mg, 0.15 mmol) and $I_2$ (800 mg, 3.1 mmol) (molar ratio 1:20) were added to freshly distilled anhydrous THF (13 mL), and the mixture was stirred at the refluxing temperature in an inert atmosphere ($N_2$) for 6 h. After cooling and addition of *n*-heptane (30 mL), the mixture was kept overnight in the refrigerator. The solid black air-stable microcrystalline material formed was then separated by centrifugation, washed with *n*-heptane until the washings were colorless, and brought to constant weight under vacuum (268 mg, yield 83%). The complex corresponds to the formula [(THF)-(TPP)Mn−N−FePc($H_2O$)]($I_5$)·2THF (**I**). Anal. Calcd for $C_{88}H_{70}FeI_5MnN_{13}O_4$: C, 49.88; H, 3.33; N, 8.59; Fe, 2.64; Mn, 2.59. Found: C, 49.80; H, 3.10; N, 8.91; Fe,2.71; Mn, 2.23%. Thermogravimetric analysis shows that **I** loses all solvent molecules (THF, $H_2O$) below 100 °C (calcd 11%, found 10.5%). At higher temperatures an almost continuous weight loss is observed due probably to iodine elimination and concomitant partial decomposition of the material.

In the synthesis of **I**, immediately after the cooling of the reaction mixture (see above), a solid precipitate could often be isolated before the addition of *n*-heptane. On the basis of elemental analyses and other data (see below), the blackish microcrystalline material, which shows an X-ray powder spectrum definitely different from that of **I**, has been assigned the formula [(TPP)Mn−N−FePc]($I_3$) (**II**). Anal. Calcd for **II**, $C_{76}H_{44}FeI_3MnN_{13}$: C, 55.98; H, 2.72; N, 11.17. Found: C, 55.81; H, 2.92; N, 10.55. In one of these oxidation reactions, 209 mg of [(TPP)-Mn−N−FePc] gave 93 mg of **II** and then 153 mg of **I**. Thermogravimetric analysis shows that **II** is stable in the range 20−90 °C. A net weight loss is observed in the range 90−220 °C, which corresponds to complete elimination of iodine (24.14%; calcd for three iodine atoms: 23.34%).

**Reaction of I and II with $NaBH_4$.** **I** (169 mg, 0.08 mmol) and $NaBH_4$ (228 mg, 6.00 mmol; molar ratio 1:75) were suspended (partly dissolved) in benzene (14 mL), and the mixture was stirred at room temperature for 24 h. The reaction product was isolated by centrifugation, washed sequentially with ethanol, $H_2O$, and ethanol, and then dried under vacuum. The IR spectrum unequivocally indicates that **I** has been totally reconverted into [(TPP)Mn−N−FePc]. An identical result is obtained by reacting **II** with $NaBH_4$ under similar experimental conditions.

**Oxidation of [(TPP)Mn−N−FePc] with (phen)$SbCl_6$ (Molar Ratio 1:1).** (phen)$SbCl_6$ (20 mg, 0.038 mmol) was dissolved in freshly distilled THF (12 mL). [(TPP)Mn−N−FePc] (46 mg, 0.037 mmol) was then added to the solution, and the mixture was stirred at room temperature in an inert atmosphere ($N_2$) for 48 h. Addition of heptane (15 mL) to the mixture and cooling overnight in a refrigerator determined the precipitation of the reaction product. The solid was separated by centrifugation, washed with *n*-heptane, and brought to constant weight under vacuum (38 mg, yield 60%). The material obtained corresponds to the formula [(THF)(TPP)Mn−N−FePc($H_2O$)]-($SbCl_6$)·2THF (**III**). Anal. Calcd for $C_{88}H_{70}Cl_6FeMnN_{13}O_4Sb$: C, 58.11; H, 3.88, N, 10.01. Found: C, 57.83; H, 3.99; N, 10.31. Thermogravimetric analysis shows a weight loss of about 11.5% due to solvent molecules, a value close to that expected (12%).

**Oxidation of [(TPP)Mn−N−FePc] with (phen)$SbCl_6$ (Molar Ratio 1:2).** [(TPP)Mn−N−FePc] (42 mg, 0.033 mmol) and (phen)-$SbCl_6$ (37 mg, 0.069 mmol) were suspended in freshly distilled benzene (12 mL), and the mixture was stirred at room temperature in an inert atmosphere ($N_2$) for 48 h. The product was separated by centrifugation of the reaction mixture, washed with *n*-pentane, and brought to constant weight under vacuum (58 mg). Elemental analyses do not lead to a precise formulation of the complex, indicating incomplete insertion of a second ($SbCl_6$)$^-$ unit. However, IR and EPR results (see the following discussion) clearly indicate that a two-electron oxidation has occurred with formation of a $\pi$-cation radical species.

**X-ray Crystallography for Complex I.** Single crystals suitable for X-ray diffraction were grown from THF/*n*-heptane. Data were collected on a Siemens AED diffractometer at 295 K using Mo Kα radiation. The solution and refinement were carried out using the programs SHELX76[15] and SHELX93.[16] Crystal data are summarized in Table 1.

---

[9] Donzello, M. P., Ercolani, C., Kadish, K. M., Ou, Z.; Russo, U. *Inorg. Chem.* **1998**, *37*, 3682.

[10] Stuzhin, P. A.; Hamdush, M.; Homborg H. *Mendeleev Comm.* **1997**, 196.

[11] Gans, P.; Marchon, J.-C.; Reed, C. A., Regnard, J.-R. *Nouv. J. Chim.* **1981**, *5*, 203.

[12] Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3964.

[13] Crystal data for compound **S1**: $C_{44}H_{28}MnN_7\cdot 0.5CHCl_3$, $M = 769.4$, orthorhombic, space group *Pccn*, $a = 21.432(3)$ Å, $b = 19.984(2)$ Å, $c = 18.432(2)$ Å, $V = 7894.4(16)$ Å$^3$, $Z = 8$, $D_{calcd} = 1.295$ g/cm$^3$, $F(000) = 3160$, $\lambda$(Mo Kα) = 0.710 69 Å, $\mu$(Mo Kα) = 4.62 cm$^{-1}$: crystal dimensions 0.10 × 0.11 × 0.27 mm. For 6226 unique observed reflections [$I > 0$] collected at $T = 295$ K on a Siemens AED ($5 < 2\theta < 56°$), the final $R$ is 0.076 (wR2 = 0.221).

[14] See the Supporting Information statement.

[15] Sheldrick, G. M. SHELX76. Program for crystal structure determination. University of Cambridge, England, 1976.

**Table 1.** Experimental Data for the X-ray Diffraction Studies on Crystalline Complex **I**

| | |
|---|---|
| formula | $[C_{80}H_{54}FeMnN_{13}O_2]^+ \cdot [I5]^- \cdot 2C_4H_8O$ |
| *a*, Å | 27.322(3) |
| *b*, Å | 12.153(2) |
| *c*, Å | 25.824(3) |
| α, deg | 90 |
| *β*, deg | 96.47(2) |
| *γ*, deg | 90 |
| V, Å$^3$ | 8520(2) |
| **Z** | **4** |
| formula weight | 2118.9 |
| space group | *Cc* (n. 9) |
| *t*, °C | 22 |
| *λ*, Å | 0.71069 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.652 |
| *μ*, cm$^{-1}$ | 21.60 |
| transmission coeff | 0.757−1.000 |
| $R^{a,b}$ | 0.050 [0.051] |
| wR$_2$ | 0.152 [0.154] |
| GOF | 0.742 [0.753] |
| *N*-observed$^c$ | 2954 |
| *N*-independent$^d$ | 9334 |
| *N*-refinement $^e$ | 7544 |
| variables | 907 |

[a] Calculated on the observed reflections having $I > 2\sigma(I)$. [b] Values in square brackets refer to the “inverted” structure. [c] *N*-observed is the total number of the independent reflections having $I > 2\sigma(I)$. [d] *N*-independent is the number of independent reflections. [e] *N*-refinement is the number of reflection used in the refinement having $I > 0$ and corrected for absorption.

The details of the X-ray data collection, structure solution, and refinement are given in the Supporting Information.[14]

**Other Physical Measurements.** IR spectra in the region 4000−200 cm$^{-1}$ were recorded on a Perkin-Elmer 783 instrument by using Nujol mulls and CsI windows. Raman spectra were run on a Spex Triplemate model 1877 spectrograph equipped with a cooled EG&G Parc model 1454 OMA detector. The exciting radiation, focused on a 5-mm Pyrex holder spinning at 1200 rpm, was provided by the 480-nm line of a Coherent model Innove 90 argon ion laser. Room-temperature magnetic susceptibility measurements were carried out by the Gouy method using a NiCl$_2$ solution as calibrant. The diamagnetic contribution of the TPP and Pc ligands were chosen as $-386 \times 10^{-6}$ and $-430 \times 10^{-6}$ cgsu/mol, respectively. Additional corrections for the solvent molecules and for iodine were calculated from Pascal’s constants. Thermogravimetric analyses were performed on a Stanton Redcroft model STA-781 analyzer under an N$_2$ atmosphere (0.5 L/min). Mössbauer spectral data were obtained as described elsewhere.[2c] Elemental analyses for C, H, N, were performed by an EA 1110 CHNS-O CE instrument, at University “La Sapienza” in Roma. Atomic absorption measurements for the quantitative detection of Fe and Mn, were made on a Varian Spectra AA-30. EPR spectra were recorded on a Varian V4502-4 spectrometer (X-band). UV−vis solution spectra were measured with a Varian Cary 5E spectrophotometer. X-ray powder patterns were obtained on a Philips mod PW 1710, CuKα Ni-filtered radiation ($\lambda = 1.540\ 51$ Å).

## Results and Discussion

**Metal- and Ligand-Centered One-Electron Oxidation of [(TPP)Mn−N−FePc] by I$_2$.** Oxidation of [(TPP)Mn−N−FePc] by I$_2$ leads to the formation of the complexes [(THF)(TPP)-Mn−N−FePc(H$_2$O)](I$_5$)·2THF (**I**) and [(TPP)Mn−N−FePc](I$_3$) (**II**). The formation of **I** and **II** determines complete disappearance of the doublet at 956−945 cm$^{-1}$, assigned as $\nu_{as}$(Mn−N−Fe), and of the strong absorption at 381 cm$^{-1}$, tentatively associated with the Mn−N−Fe bond system ($\nu_s$(Mn−N−Fe)),[9] found present in the IR spectrum of the precursor [(TPP)Mn−N−FePc]. The observed IR spectral changes are useful for the control of the total conversion of (TPP)Mn−N−FePc into **I** and **II** and resemble those observed in the one-electron oxidation of the *μ*-nitrido species [PcFe−N−FePc][2c] and [(TPP)Fe−N−FePc].[6] The above absorptions reappear in the IR spectrum, once **I** and **II** are brought back to [(TPP)Mn−N−FePc] by reduction with NaBH$_4$ (see the Experimental Section).

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Complex **I**

| | | | |
|---|---|---|---|
| I(1)−I(2) | 2.790(2) | Fe(1)−N(15) | 1.970(11) |
| I(2)−I(3) | 3.274(2) | Fe(1)−N(17) | 1.992(11) |
| I(3)−I(4) | 3.023(2) | Mn(1)−O(1) | 2.200(10) |
| I(4)−I(5)A | 2.972(3) | Mn(1)−N(1) | 2.009(11) |
| I(4)−I(5)B | 2.774(3) | Mn(1)−N(2) | 2.015(11) |
| Fe(1)−O(2) | 2.116(9) | Mn(1)−N(3) | 2.033(11) |
| Fe(1)−N(10) | 1.683(12) | Mn(1)−N(4) | 2.016(11) |
| Fe(1)−N(11) | 1.970(11) | Mn(1)−N(10) | 1.669(12) |
| Fe(1)−N(13) | 1.955(11) | | |

| | | | |
|---|---|---|---|
| I(1)−I(2)−I(3) | 176.3(1) | O(2)−Fe(1)−N(10) | 179.7(5) |
| I(2)−I(3)−I(4) | 88.4(1) | N(4)−Mn(1)−N(10) | 94.4(5) |
| I(3)−I(4)−I(5)B | 178.5(1) | N(3)−Mn(1)−N(10) | 93.6(5) |
| I(3)−I(4)−I(5)A | 166.7(1) | N(3)−Mn(1)−N(4) | 90.0(4) |
| N(15)−Fe(1)−N(17) | 88.0(4) | N(2)−Mn(1)−N(10) | 93.4(5) |
| N(13)−Fe(1)−N(17) | 174.6(5) | N(2)−Mn(1)−N(4) | 172.2(4) |
| N(13)−Fe(1)−N(15) | 91.1(4) | N(2)−Mn(1)−N(3) | 89.2(4) |
| N(11)−Fe(1)−N(17) | 91.8(4) | N(1)−Mn(1)−N(10) | 94.4(5) |
| N(11)−Fe(1)−N(15) | 174.1(5) | N(1)−Mn(1)−N(4) | 88.7(4) |
| N(11)−Fe(1)−N(13) | 88.6(4) | N(1)−Mn(1)−N(3) | 172.1(4) |
| N(10)−Fe(1)−N(17) | 92.7(5) | N(1)−Mn(1)−N(2) | 91.0(4) |
| N(10)−Fe(1)−N(15) | 93.4(5) | O(1)−Mn(1)−N(10) | 178.9(5) |
| N(10)−Fe(1)−N(13) | 92.7(5) | O(1)−Mn(1)−N(4) | 86.6(4) |
| N(10)−Fe(1)−N(11) | 92.5(5) | O(1)−Mn(1)−N(3) | 85.9(4) |
| O(2)−Fe(1)−N(17) | 87.2(4) | O(1)−Mn(1)−N(2) | 85.6(4) |
| O(2)−Fe(1)−N(15) | 86.9(4) | O(1)−Mn(1)−N(1) | 86.2(4) |
| O(2)−Fe(1)−N(13) | 87.4(4) | Mn(1)−N(10)−Fe(1) | 178.6(7) |
| O(2)−Fe(1)−N(11) | 87.2(4) | | |

**(i) Structural and Electronic Features of I.** The structure of **I** consists of (a) a cationic fragment formed by the two units [(THF)Mn(TPP)] and [Fe(Pc)(H$_2$O)] held together by the bridging N(10) atom, as shown in Figures 1 (side view) and 2 (top view); (b) a (I$_5$)$^-$ counterion; and (c) two hydrogen-bonded THF molecules. The two M−N$_4$ cores in the cationic fragment are planar (the metal displacements are 0.138(2) and 0.097(2) Å for Mn and Fe, respectively) and parallel to each other, the dihedral angle between them being 1.07(3)°. The mean Mn(1)−N(10)−Fe(1) line is perpendicular to the M−N$_4$ cores, the dihedral angles formed with the normal to the MnN$_4$ and FeN$_4$ systems being 0.7(4) and 0.4(4)°, respectively. Each metal exhibits a distorted octahedral coordination, with the related N$_4$ core defining the equatorial plane and the N(10), O(1) and N(10), O(2) the donor atoms ligated at the axial positions of Mn and Fe, respectively.

Complex **I** is isostructural with the corresponding Fe−Fe complex previously described in detail.[6] Hence, specific comments for the present species will be essentially confined here to the structural features of the immediate environment of the Mn−N−Fe bond system. Some of the selected bond distances and angles for **I** are listed in Table 2. The metal−N(10) bond distances in **I** (Fe−N(10), 1.683(12) Å; Mn−N(10), 1.669(12) Å) are indicative of consistent *π*-electron conjugation running along the Mn−N−Fe bridge, definitely confirming its previously suggested[9] and now definitely established linearity (178.6(7)°). The same distances for **I** and those of the Fe−Fe analogue (Fe(1)−N(10) = 1.652(2) Å; Fe(2)−N(10) = 1.63(2) Å) are all in the narrow range 1.63−1.682 Å (Table 2), clearly indicating the presence of M═N(10) double bonds and suggesting the occurrence of a Mn$^{IV}$═N═Fe$^{IV}$ triatomic fragment. In fact,

---

(16) Sheldrick, G. M. SHELXL93. Program for crystal structure refinement. University of Göttingen, Germany, 1993.

**Table 3.** Low-Temperature (78 K) Mössbauer Data for **I**, **II**, and Other Related Species

| complex | $\delta^a$ (mm sec$^{-1}$) | $\Delta E_Q$ (mm s$^{-1}$) | $\Gamma^b$ (mm s$^{-1}$) | ref$^c$ |
|---|---|---|---|---|
| [(TPP)Mn−N−FePc] | 0.19 | 1.21 | 0.13 | 9 |
| [(THF)(TPP)Mn−N−FePc($H_2O$)($I_5$)·2THF (**I**) | −0.01 | 1.98 | 0.18 | tp |
| (**I**)$ClO_4$ (34%) | −0.02 | 2.64 | 0.25 | 9 |
| (**I**)$ClO_4$ (29%) | 0.00 | 1.99 | 0.24 | |
| (**I**)$ClO_4$ (37%) | −0.01 | 1.29 | 0.25 | |
| [(THF)(TPP)Fe−N−FePc($H_2O$)($I_5$)·2THF | −0.05 | 1.99 | 0.16 | 6 |
| [(TPP)Mn−N−FePc]($I_3$) (**II**) | 0.18 | 1.13 | 0.17 | tp |

[a] Referred to metallic iron. [b] Half-width at half-maximum height. [c] tp = this paper.

although there are no X-ray data reported in the literature on strictly related $\mu$-nitrido Mn derivatives, 66 entries in the literature of Mn═N bond distances give values ranging from 1.553 to 1.791 Å, with an average value of 1.660(7) Å, practically coincident with that observed for **I**. More closely, the Mn−N bond distance is much shorter than the Mn(1)−N(5) single-bond distance (2.035(6) Å) observed in the five-coordinate (TPP)MnN$_3$(CHCl$_3$)$_{0.5}$ (see complex S1 in the Supporting Information) and (TPP)MnN$_3$·C$_6$H$_6$[17] (2.045(4) Å) and in the six-coordinate [(TPP)Mn(N$_3$)(CH$_3$OH)][18] (2.176(9) Å), while, on the other hand, it is significantly longer than that found for the Mn≡N triple bond in the nitrido species (TTP)-MnN (1.515 Å)[19] and (OEPMe$_2$)MnN (1.512(2) Å).[20] Indicative of a M−N double bond is also the Fe(1)−N(10) bond distance (1.663(12) Å), found closely approaching the corresponding values for the Fe(IV)−Fe(IV) analogue (1.63(2) and 1.65(2) Å),[6] and those of other Fe(IV)−X−Fe(IV) ditetrapyrrolic species (X = N, C),[7,8,21−23] The metal−N$_{(TPP,Pc)}$ bond distances, mean values 2.018(13) and 1.972(13) Å for Mn−N$_{(TPP)}$ and Fe−N$_{(Pc)}$, respectively, as well as the axial external metal-O bond distances, are all in the expected ranges and deserve no further comments.

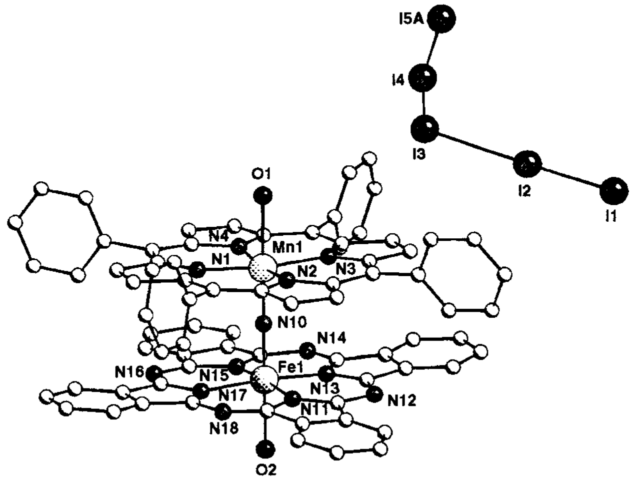

**Figure 1.** SCHAKAL side view of complex **I**. THF molecules and disorder affecting the $I_5^-$ anion have been omitted for clarity.

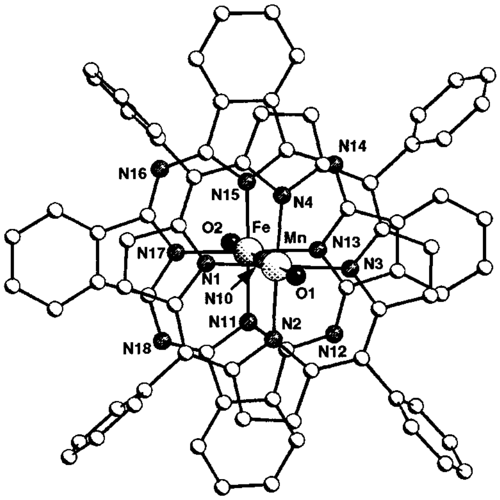

**Figure 2.** SCHAKAL top view of the cation in complex **I**. The carbon atoms of the THF molecule bonded to manganese have been omitted for clarity.

The $I_5^-$ anion shows an uneven V-shaped geometry. Bond distances and angles (Table 2) suggest an ($I_2$)($I_3^-$) arrangement, analogous to that observed for the Fe−Fe analogue,[6] and further confirmed by the Raman spectrum which shows one peak at 170 cm$^{-1}$ ($I_2$), and peaks at 141.2 and 109.6 ($I_3^-$). Two THF solvent molecules approach the [Fe(Pc)($H_2O$)] unit pointing the oxygen atoms toward the oxygen atom of the bound water molecule. Although the hydrogen atoms for the water molecule could not be localized, the values of the contact distances (O(2)···O(3), 2.69(2) Å; O(2)···O(4), 2.738(19) Å) are consistent with the presence of hydrogen bonds.

Mössbauer spectral data for **I** are summarized in Table 3, together with those of strictly related species. The spectrum of **I** shows a clean doublet with an isomer shift close to zero (− 0.01 mm/s), which is far lower that of its precursor [(TPP)-Mn−N−FePc] ($\delta$ = 0.19 mm/s), for which indications were given for the occurrence of an electronic charge distribution very close to that expected for a couple Mn(IV)−Fe(III),[9] and also lower than that of [(TPP)Fe−N−FePc] ($\delta$ = 0.11 mm/s)[5] containing two equivalent Fe(III$^1/_2$) centers, and, therefore, undoubtedly suggesting the presence of Fe(IV). Moreover, this value is practically coincident with the value observed for the Fe(IV)-containing analogue [(THF)(TPP)Fe−N−FePc($H_2O$)]-($I_5$)·2THF.[6] Conclusively, then, the one-electron oxidation of [(TPP)Mn−N−FePc] to **I** occurs at the Mn−N−Fe site, i.e., is metal-centered, confirming the presence of the Mn(IV)−Fe-(IV) couple, in keeping with X-ray structural information. The room temperature $\mu_{\mathrm{eff}}$ value for **I** is 1.85 $\mu_B$, which establishes that the d$^3$-d$^4$ system is low-spin. The EPR spectrum of **I** is reported in Figure 3; associated parameters are given in Table 4. The spectrum, closely resembling that of the “perchlorate” obtained by oxidation of [(TPP)Mn−N−FePc] with perchloric acid,[9] shows a well resolved hyperfine structure indicative of the presence of the unpaired electron along the Mn−N−Fe bond

---

(17) Day, V. W.; Stults, B. R.; Tasset, E. L.; Marianelli, R. S.; Boucher, L. J. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 505.

(18) (a) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2650. (b) Stults, B. R.; Day, V. W.; Tasset, E. L.; Marianelli, R. S. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1259.

(19) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318.

(20) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Scheidt W. R. *Inorg. Chem.* **1983**, *22*, 888.

(21) Moubaraki, P. A.; Benlian, D.; Baldy, A.; Pierrot, M. *Acta Crystallogr.* **1989**, *C45*, 393.

(22) Rossi, G.; Goedken, V. L.; Ercolani, C. *J. Chem. Soc., Chem. Commun.* **1988**, 46.

(23) Galich L.; Kienast, A.; Hückstädt, H.; Homborg, H. *Z. Anorg. Allg Chemie* **1998**, *624*, 1235.

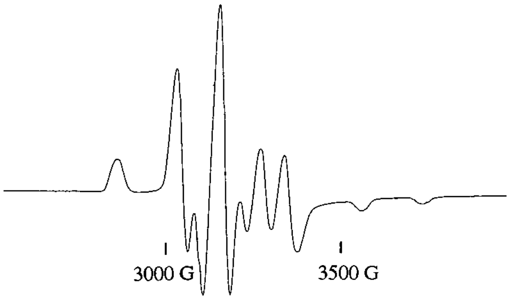

**Figure 3.** EPR spectrum of I at 78 K.

**Table 4.** EPR Data on I and Related Species

| complex | $g_{\parallel}$ | $g_{\perp}$ | $A_{\parallel}$ (G) | $A_{\perp}$ (G) |
|---|---|---|---|---|
| **I** | 1.972 | 2.037 | 177.5 | 63 |
| "perchlorate"[a] | 1.980 | 2.038 | 179 | 64.5 |
| **III** | 1.973 | 2.036 | 177.5 | 63.5 |

[a] Reference 9.

system and strongly interacting with the nuclear spin of the Mn atom (natural abundance 100% $^{55}$Mn, nuclear spin 5/2). The large A values observed, practically identical to those of the "perchlorate", suggest that the electron is mainly spending its time in the surroundings of the Mn atom.

**(ii) Complex II: Ligand-Centered One-Electron Oxidation.** As mentioned above, complex **II**, i.e., [(TPP)Mn−N−FePc]($I_3$), is occasionally formed, together with **I**, by the reaction of [(TPP)Mn−N−FePc] with $I_2$. Information available, based on EPR, Mössbauer, Raman, and IR data, indicates that in this species oxidation is ligand-centered, in contrast with the results for **I**. The EPR spectrum of **II** is dominated by an intense isotropic peak with a $g$ value of 2.003 ($\Delta H = 11$ G), typical of an organic radical species, accompanied by a low intensity hyperfine structure, very likely due to traces of **I**. Noticeably, the Mössbauer spectral data (Table 3) are practically coincident with those of the starting species [(TPP)Mn−N−FePc], indicating that formation of **II** has not significantly affected the electronic situation of the Fe center and of the entire Mn−N−Fe site either. Finally, the IR spectrum of **II** shows an absorption of medium intensity at 1360 cm$^{-1}$ absent in the IR spectra of **I** and its precursor [(TPP)Mn−N−FePc]. This absorption can be taken as indicative of the presence of the TPP radical.[24] In the case of the formation of a Pc radical, on the other hand, an IR absorption would be found normally in the region 1100−1150 cm$^{-1}$.[25] Noteworthy, there are no solvent molecules coordinated on the two metal centers in the cationic species [(TPP)Mn−N−FePc]$^{+\cdot}$. This is indicative of the fact that the Lewis acidity of the two metal centers has not changed significantly, this avoiding axial ligation of THF or $H_2O$ molecules as occurs in the case of **I** (metal-centered oxidation). The Raman spectrum of **II** shows a very intense peak at 168 cm$^{-1}$ ($I_2$) and only a very weak peak at 107 cm$^{-1}$. This means that the $I_3^-$ anion should be rather formulated as a $I_2\cdots I^-$ moiety.

**Reaction of I with (phenox)SbCl$_6$ (Molar Ratios 1:1 and 1:2).** Reaction of [(TPP)Mn−N−FePc] with (phen)SbCl$_6$ (molar ratio 1:1) leads to a dark gray microcrystalline powder corresponding to the formula [(THF)(TPP)Mn−N−FePc($H_2O$)]($SbCl_6$)·2THF (**III**). Thermogravimetric analysis shows a net weight loss in the range 80−100 °C, indicating elimination of solvent molecules (THF, see the Experimental Section). The IR spectrum of **III** is practically identical to that of **I**, except for the presence of an intense absorption at 345 cm$^{-1}$ due to the $SbCl_6^-$ ion. Its EPR spectrum shows a hyperfine structure, general features, and associated parameters (Table 4) quite similar to those of **I**, suggesting, as for the latter, a metal-centered oxidation, with formation of the bond system $Mn^{IV}{=}N{=}Fe^{IV}$ and an unpaired electron mainly residing in the proximity of the Mn atom.

The stable-to-air blackish brown powder obtained from **I** and (phenox)SbCl$_6$ when they are made to react in benzene in a 1:2 molar ratio could not be given a precise formulation because of the poor elemental analyses. Its IR spectrum appears quite different from that of **III** and makes difficult the assignment of absorptions possibly associated with the presence of $\pi$-cation radicals. For this, more indicative is its EPR spectrum, which shows a single intense signal (width 47 G) at $g = 2.0183$. At high resolution the spectrum evidences also the hyperfine structure of the type already observed for the species **I** and **III**. Whether or not this is due to an impurity or to the concomitant occurrence in a single species of metal- and ligand-centered oxidations is being the object of further investigation.

**Acknowledgment.** This work was financed by the Italian grant Murst Cofin-9903263473. The authors are very grateful to Prof. P. Deplano (University of Cagliari) and Dr. D. Attanasio (Area della Ricerca di Montelibretti, CNR) for useful discussions on the Raman and EPR spectra. Thanks are addressed to Dr. P. Galli (Chemistry Department, University "La Sapienza") for elemental analyses (C, H, N) and to Dr. R. Dragone for quantitative detection of Mn and Fe by atomic absorption and X-ray powder patterns.

**Supporting Information Available:** SCHAKAL and ORTEP diagrams and tables giving crystal data and structure refinement details, atomic coordinates, isotropic and anisotropic displacement parameters, and bond length and angles for complexes **I** and **S1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000874M

---

(24) Shimomura, E. T.; Philippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

(25) Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461.