*Inorg. Chem.* **1993**, *32*, 2975-2977 **2975**

# First Example of a Mixed-Ligand Bimetallic (Fe–Fe) N-Bridged Dimer: (μ-Nitrido)[((tetraphenylporphyrinato)iron)-(phthalocyaninato)iron]

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*Received November 6, 1992*

## Introduction

The number of known nitrogen-bridged bimetallic systems containing the skeleton M–N–M (M being a metal ion, externally coordinatively saturated with mono- or multidentate ligands) is quite restricted, expecially if compared with the large number of analogous known μ-oxo dimers.[1] Even more restricted is the number of N-bridged dimers of formula (L)M–N–M(L), with L being a macrocyclic dianionic $N_4$ chromophore and M a transition metal ion, which include a few Fe–porphyrin[2] and Fe–phthalocyanine derivatives[3] and one Ru–phthalocyanine complex, i.e. $(PcRu)_2N$.[4]

No examples are known in the literature of μ-nitrido dimers carrying different dianionic macrocyclic rings (the above mentioned $N_4$ chromophores or similar multidentate dianionic ligands), (L)M–N–M(L′), or even containing different metal ions, as in the series (L)M–N–M′(L) and (L)M–N–M′(L′). One possible route to the synthesis of this kind of complexes might imply the use of the decomposition reaction of a monomeric azide $(L)MN_3$ in presence of the appropriate co-reactant. By this way we have accomplished the synthesis of the porphyrin–phthalocyanine mixed-ligand complex TPPFe–N–FePc, starting from (TPP)Fe$^{\mathrm{III}}$N$_3$ and PcFe$^{\mathrm{II}}$. The question arising for this complex is whether it should be given one of the alternative formulations (TPP)Fe$^{\mathrm{IV}}$–N–Fe$^{\mathrm{III}}$Pc and (TPP)Fe$^{\mathrm{III}}$–N–Fe$^{\mathrm{IV}}$Pc or, despite the different environmental situation for the two metal ions, it should be assigned the formula TPPFe$^{\mathrm{III}\,1/2}$–N–Fe$^{\mathrm{III}\,1/2}$Pc, as has been found for $(PcFe)_2N$ and $(TPPFe)_2N$ (ref 3b, and references therein). This problem is discussed here on the basis of IR, Mössbauer, EPR, and magnetic susceptibility data.

## Experimental Section

PcFe (Eastman Kodak) was purified by vacuum sublimation at 400 °C under vacuum ($10^{-2}$ mmHg). ((TPP)Fe)$_2$O was used as purchased from Strem Chemicals. Xylene was refluxed in presence of $CaH_2$ and distilled before use. Other solvents and chemicals were reagent grade and used without further purification.

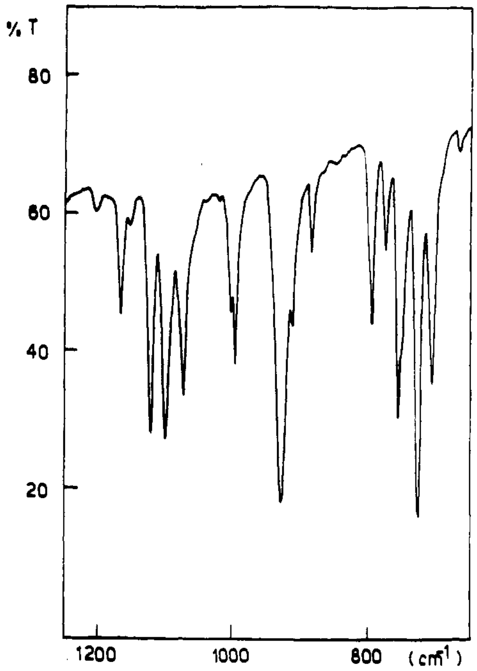

**Figure 1.** IR spectrum of S in the region 1250–650 cm$^{-1}$.

**(TPP)FeN$_3$.** This compound was prepared, slightly changing the procedure reported elsewhere,[5] in the following way.

$NaN_3$ (5.75 g, 0.888 mol), dissolved in $H_2O$ (75 mL), was passed through a cation exchange column (Bio-rad AG 50W-X$_2$, 100–200 mesh, wet column 125 mL). The resultant hydrazoic acid solution (50 mL) was shaken vigorously with a solution of ((TPP)Fe)$_2$O (250 mg, 0.185 mmol) in freshly distilled benzene (150 mL) for 20 min. The reaction mixture was allowed to stand. The aqueous layer was discarded, and the benzene layer was washed three times with equal volumes (100 mL) of water. The benzene layer was dried over anhydrous $Na_2SO_4$, separated by filtration, and evaporated to dryness. The solid residue obtained was then brought to constant weight under vacuum at room temperature (234 mg, 89%). Anal. Calcd. for $C_{44}H_{28}N_7Fe$: C, 74.37; H, 3.97; N, 13.80. Found: C, 74.70; H, 3.95; N, 13.84.

**Synthesis of TPPFe–N–FePc.** PcFe (96 mg, 0.17 mmol) was added to a suspension of finely ground (TPP)FeN$_3$ (180 mg, 0.255 mmol; partially dissolved) in xylene (20 mL). The mixture was refluxed at 120 °C (carefully controlled), under $N_2$, with constant stirring, for 8 h. The reaction mixture was allowed to cool to room temperature and xylene was separated, after centrifuging, from the solid residue, which was then washed with xylene until the washings were light green in color and excess of the unreacted TPP complex was completely eliminated. The solid blue microcrystalline material was dried under vacuum at room temperature (160 mg, 65%). Anal. Calcd. for (TPP)Fe–N–FePc, $C_{76}H_{44}N_{13}Fe_2$: C, 72.97; H, 3.55; N, 14.56. Found: 72.15; H, 3.51; N, 14.39. It is insoluble in water and in nondonor organic solvents, but sparingly soluble in $CH_2Cl_2$, $CHCl_3$, and pyridine with some changes, as indicated by visible solution spectra.

**Physical Measurements.** Thermogravimetric analyses were performed on a Stanton Redcroft Model STA-781 analyzer. IR spectra in the region 4000–200 cm$^{-1}$ were taken on a Perkin-Elmer 783 instrument as nujol mulls, using CsI plates. Mössbauer spectral data were obtained as described elsewhere.[6] EPR spectra were recorded on a Varian V4502-4 spectrometer (X-band) at 110 K. UV–visible solution spectra were recorded on a Perkin-Elmer Model 555 spectrophotometer. Room-temperature magnetic susceptibility measurements were obtained by the Gouy method. The diamagnetic contribution of the ligands was chosen as −386 × 10$^{-6}$ and −430 × 10$^{-6}$ cgsu/mol for the TPP and Pc ligands, respectively.

## Results and Discussion

The reaction conditions found for the synthesis of (TPP)Fe–N–FePc (hereafter indicated as S) from (TPP)FeN$_3$ and PcFe

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(4) Rossi, G.; Gardini, M.; Pennesi, G.; Ercolani, C.; Goedken, V. L. *J. Chem. Soc., Dalton Trans.* **1989**, 193. Abbreviations used in the present paper: Pc = phthalocyaninato anion, $[C_{32}H_{16}N_8]^{2-}$; TPP = tetraphenylporphyrinato anion, $[C_{44}H_{28}N_4]^{2-}$.

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**Table I.** IR, Mössbauer, and EPR Data for $\mu$-X Fe–Fe Systems

| complex | $\nu_{as}$ (cm$^{-1}$) | $\delta^{a}$ (mm/s) | $\Delta E_Q$ (mm/s) | $g_\perp$ | $g_\parallel$ | refs |
|---|---|---|---|---|---|---|
| (TPP)Fe–N–FePc (S) (spectrum A) | 930 vs | 0.11$^{b}$ | 1.47 | 2.099 | 2.005 | this work |
| | | 0.13$^{d}$ | 1.45 | | | this work |
| (TPP)Fe–N–FePc (S + impurity, spectrum B) | | –0.02$^{b}$ | 1.57 | | | this work |
| | | 0.63$^{b}$ | 2.22 | | | this work |
| ((TPP)Fe)$_2$N | 910 vs–885 m | 0.18$^{c}$ | 1.08 | 2.15 | 2.01 | 5, 10, 13 |
| (PcFe)$_2$N | 915 vs | 0.06$^{b}$ | 1.76 | 2.13 | 2.03 | 3a,b, 6, 11 |
| ((TPP)Fe)$_2$O | 885 m–870 s | 0.40$^{c}$ | 0.62 | | | 14 |
| | 892 m–878 s | | | | | 15 |
| (PcFe)$_2$O [$\mu$-Oxo(1)] | 852 s–824 s | 0.36$^{b}$ | 0.44 | | | 16, 17 |
| ((TPP)Fe)$_2$C | 940 vs–883 sh | 0.10$^{c}$ | 1.88 | | | 7, 10 |
| (PcFe)$_2$C | 990 vs | –0.16$^{b}$ | 2.69 | | | 18, 19 |

$^{a}$ Referred to the Fe metal;$^{b-d}$ Mössbauer data taken at 77, 131, and 4 K, respectively

were appropriately selected (120 °C, 8 h, inert atmosphere) in order to drive the reaction to the formation of a pure crystalline material. It was observed, in fact, that temperatures below 120 °C, as also times shorter than 8 h, do not favor the complete conversion of the reactants into the final products. Higher temperatures, on the other hand, often caused the formation of ((TPP)Fe)$_2$N as impurity, as indicated elsewhere.[5] The inert atmosphere is necessary, since in the presence of air both $\mu$-oxo dimers, i.e. ((TPP)Fe)$_2$O and (PcFe)$_2$O, are also formed as impurities. Lower ratios of the reactants ((TPP)FeN$_3$:PcFe), with respect to that used for the synthesis (1.5:1), can determine the formation of minor amounts of an additional species, whose the presence is clearly shown by the Mössbauer spectrum of the bulk material (see below). This impurity would then be difficult to eliminate, due to solubility problems.

S, as a solid, is indefinitely stable in air at room temperature. Thermogravimetric analysis under nitrogen indicates no weight loss occurring up to temperatures of ca. 350 °C, with the residue still essentially unchanged, as shown by its IR spectrum. The sublimation conditions for S (10$^{-2}$ mmHg, 400–450 °C) leave the residue essentially unchanged. The sublimed material, instead, consists of distinct TPP and Pc species showing the presence of some ((TPP)Fe)$_2$O and PcH$_2$, and, thus, indicating the breaking of the N-bridged dimer during sublimation.

The IR spectrum of S shows the complete absence of the intense band at 2053 cm$^{-1}$ of the azide group present in (TPP)FeN$_3$. The spectrum exhibits absorptions typical of both TPP and Pc skeletons, appearing of comparable intensity in all the region explored. Figure 1 shows the IR spectrum of S in the region 1250–650 cm$^{-1}$. The very intense absorption located at 930 cm$^{-1}$, and not present in the starting materials, is assigned as $\nu_{as}$(Fe–N–Fe). Table I summarizes the $\nu_{as}$(Fe–X–Fe) values observed for S and other strictly related species. Noticeably, $\nu_{as}$ for S is higher than the corresponding values observed for both the $\mu$-nitrido species ((TPP)Fe)$_2$N (910 vs, 885 m cm$^{-1}$)[5] and (PcFe)$_2$N (915 cm$^{-1}$),[3a,b] which seems to indicate a higher degree of reinforcing $\pi$-bond character present in the Fe–N–Fe bond system for S. Since X-ray single-crystal work has established that the trinuclear Fe–N–Fe moiety is linear in ((TPP)Fe)$_2$N,[2a] and a linear arrangement has been also sufficiently proven for (PcFe)$_2$N,[3a,b] the same must be true for S, in keeping with the IR features. Moreover, $\nu_{as}$(Fe–N–Fe) for S is in between the values observed for the analogous $\mu$-oxo and the $\mu$-carbido species, as is reasonably predictable; noticeably, however, its position is very close to that of the $\mu$-carbido species ((TPP)Fe)$_2$C (940 cm$^{-1}$, vs, with shoulder at 883 cm$^{-1}$),[7] which is also in keeping with the presence of a consistent degree of $\pi$-bond character in S. Since (TPPFe)$_2$C,[8] as also the six-coordinate $\mu$-carbido species [(1-meim)PcFe]$_2$C,[9] are known to have a linear Fe–C–Fe bond system from X-ray work, there appears to be little doubt, then, about the occurrence of a linear array for the Fe–N–Fe moiety in S. This, in turn, is in favor of an efficient electronic and magnetic exchange for the two Fe atoms through the bridging N atom.

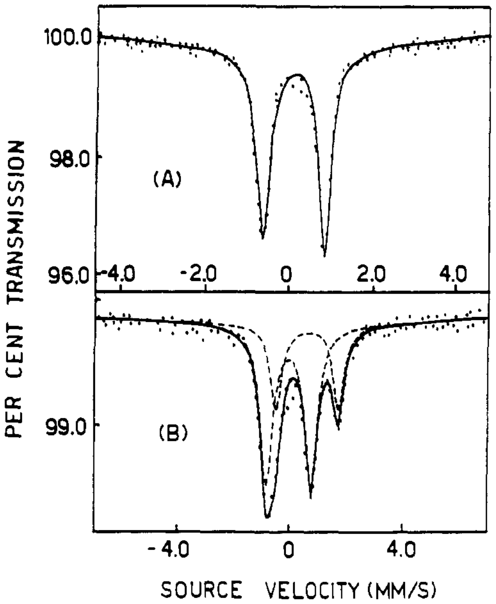

**Figure 2.** Mössbauer spectra of S (A) and S plus unknown impurity (B).

The Mössbauer spectrum of a sample of pure S is given in Figure 2A, together with that of a sample containing S and the impurity present when no excess of (TPP)FeN$_3$ is used for the synthesis (Figure 2B). The pertinent $\delta$ and $\Delta E_Q$ values are given in Table I, together with the corresponding values of similar systems. The Mössbauer spectrum of pure S shows a single clean quadrupole doublet, indicative of the presence of only one type of Fe atoms within the dimer, at least within the time scale of the measurement (10$^{-7}$ s). The observed isomer shift and quadrupole splitting values for S are 0.113 mm/s and 1.467 mm/s, respectively (slightly different values are observed for the impure sample of Figure 2B, as caused by the independent fitting of the spectrum). From Table I it can be seen that both values are just in between those found for ((TPP)Fe)$_2$N[10] and (PcFe)$_2$N[6,11]. As for both these latter species, the oxidation state of the Fe centers in S must be assumed to be intermediate between 3 and 4, i.e. 3.5. If this interpretation is correct, then, evidently, the electronic exchange occurring between the two Fe centers in S neutralizes the effects of the different ligand fields produced on them by the TPP and Pc macrocyclic rings.

((TPP)Fe)$_2$N[12] and (PcFe)$_2$N[3a,b,6] were assigned a low-spin

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electronic configuration with one unpaired electron per dimer; this might suggest a similar assignement also for S, if account is taken of the intermediate Mössbauer values measured. This assignement is supported for S by its esr spectrum, which exhibits features similar to those observed for $(\mathrm{TPPFe})_2\mathrm{N}$[13] and $(\mathrm{PcFe})_2\mathrm{N}$[3b]. In fact, the spectrum shows some anisotropy, with $g_\perp$ and $g_\parallel$ values of 2.099 and 2.005, respectively. A hyperfine $^{14}\mathrm{N}$ ($I = 1$) structure is present on both $g$ values, proving that the unpaired electron is essentially localized on the Fe–N–Fe bond system with significant N atom character.

Magnetic susceptibility studies on the $\mu$-oxo–Fe–phthalocyanine dimers have proved useful in identifying the degree of magnetic exchange between the two Fe centres and the spin state of the metal. Less informative were the magnetic data on $((\mathrm{TTP})\mathrm{Fe})_2\mathrm{N}$[7] and $(\mathrm{PcFe})_2\mathrm{N}$,[6] although substantially identifying the low-spin state of these bimetallic systems. Room-temperature magnetic susceptibility measurements on different samples gave for S $\mu_{\mathrm{eff}}$ values in the range 2.5–3.0 $\mu_{\mathrm{B}}$, not in contrast with the presence of one unpaired electron per dimer. The observed variability, which did not allow a detailed magnetic study, has to be assigned most likely to the presence of paramagnetic impurities, as often occurs for these type of complexes.

The Mössbauer spectrum of Figure 2B indicates the presence of an additional species present as contaminant (ca. 33%), very likely derived from PcFe, and with isomer shift and quadrupole splitting values of 0.63 and 2.22 mm/s, respectively. These values, which are different from those of PcFe, $(\mathrm{PcFe})_2\mathrm{O}$, or $(\mathrm{PcFe})_2\mathrm{N}$, do not allow an easy identification of the impurity.

**Acknowledgment.** The authors are grateful to Prof. U. Russo for help with the Mössbauer measurements. R.H. and S.H. acknowledge grants by the Deutsche Forschungsgemeinschaft and by the Italian CNR, respectively. Thanks are addressed by these authors to the Dipartimento di Chimica, Università "La Sapienza", Roma, for kind hospitality. Financial support by the Consiglio Nazionale delle Ricerche is gratefully acknowledged. The authors thank the Servizio di microanalisi, Area della Ricerca di Roma, CNR (F. Dianetti, L. Petrilli), for elemental analyses.

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