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(μ-Nitrido)((tetraphenylporphyrinato)iron)((phthalocyaninato)iron) and Its Fe−Ru Analogue: Redox Behavior and Characterization of New Fe(IV)-Containing Species. X-ray Crystal Structure of [(THF)(TPP)Fe−N−FePc(H_2O)](I_5)·2THF

C. Ercolani,*,† J. Jubb,† G. Pennesi,*,‡ U. Russo,§ and G. Trigiante†

Dipartimento di Chimica, Università di Roma La Sapienza, Roma, Italy, ICMAT (CNR), Area della Ricerca di Roma, Monterotondo Scalo, Italy, and Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Padova, Italy

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The mixed-ligand bimetallic N-bridged, formally mixed-valence Fe(III)−Fe(IV) species (TPP)Fe−N−FePc, previously reported, and the heterobimetallic analogue (TPP)Fe−N−RuPc have been prepared and characterized, and their redox properties have been examined. Oxidation of these species with I_2 leads in both cases to monopositively charged Fe−Fe and Fe−Ru μ-nitrido dimers, having I_5^- as counterion. By reaction with $NaBH_4$, these salt-like species are reduced to the starting materials. The structure of the complex [(THF)(TPP)Fe−N−FePc(H_2O)](I_5)·2THF has been elucidated by an X-ray study. The complex crystallizes in the monoclinic system. Unit cell data: formula $C_{88}H_{70}Fe_2I_5N_{13}O_4$, $M = 2119.94$, $a = 27.13(1)$ Å, $b = 12.032(5)$ Å, $c = 25.596(41)$ Å, $V = 8298(20)$ Å^3, $Z = 4$, space group *Cc*. The structure shows that the phthalocyanine and tetraphenylporphyrin rings are held together by the nearly linear triatomic Fe−N−Fe moiety (179°). Each Fe atom within the molecule lies in the plane of the respective macrocycle, six-coordination being achieved by external axial ligation of H_2O and THF molecules at the PcFe and (TPP)Fe sites, respectively. The H_2O molecule is hydrogen-bonded to two additional THF molecules. The I_5^- ion is V-shaped and lies separately in the crystal. Additional information on the molecular and electronic structure of the present Fe−Fe and Fe−Ru species has been obtained from IR, Raman, Mössbauer, and EPR spectra and also from magnetic susceptibility data.

Introduction

We recently reported the synthesis and characterization of the first example of a mixed-ligand μ-nitrido bimetallic dimer, (TPP)Fe−N−FePc, corresponding to the general formula (L)M−N−M(L′), L and L′ being different macrocyclic N_4 rings (the terms "dimer" or "dimers" for these and similar species, although strictly incorrect, are used here for convenience).[1] This formally mixed-valence [Fe(III)−Fe(IV)] dimer actually shows the two metal centers to have the same oxidation state (within the time scale of a Mössbauer experiment), i.e. Fe(III$^{1/2}$), this clearly showing that the effect due to the different ligand field strength of the two macrocyclic rings on the respective metal ions is overcome by the mediating action of the N atom bridging the two Fe centers. We report here the synthesis and characterization of a similar μ-nitrido species, which represents the first example of a new class of complexes of formula (L)M−N−M′(L′), i.e. (TPP)Fe−N−RuPc, in which the two metal centers are also different. The oxidation reaction of both these Fe−Fe and Fe−Ru species with I_2 results in the formation of salt−like species which contain the monoelectrically oxidized μ-nitrido cation neutralized by the I_5^- anion. The molecular and electronic structure of both nonoxidized and oxidized species is discussed on the basis of X-ray work and other chemical−physical information. This work extends the number of Fe(IV)-containing species belonging to the above mentioned classes of bimetallic systems.

Experimental Section

PcFe was prepared from phthalodinitrile and $Fe(CO)_5$ by following a reported method.[2] Alternatively, PcFe was purchased from Eastman-Kodak. If necessary, samples were purified by sublimation under vacuum (400−450 °C, 10^{-2} mmHg). $(PcRu)_2$[3] was obtained from pure [PcRu(DMSO)$_2$](DMSO)$_2$ as described elsewhere[4] and also as followed by us.[3,5] (TPP)FeN_3 was prepared from (TPP)FeCl, and this, in turn, from $TPPH_2$, all being obtained by following procedures previously described.[6−8] Twice-sublimed I_2 from Carlo Erba was used as such. $NaBH_4$ was a pure reagent from Fluka. THF was made anhydrous by refluxing it over potassium and freshly distilled before use. Pentane, heptane, acetone, ether, and benzene, from Carlo Erba, Fluka, or Aldrich, were pure solvents and were used without further purification.

(TPP)Fe−N−FePc (Hereafter Indicated as μ-N). The synthesis of this complex in xylene was previously described.[1] Alternatively, it can be obtained in ClNP, by the following similar procedure.

(TPP)FeN_3 (1.5 g, 2.1 mmol) and PcFe (1.2 g, 2.1 mmol) were suspended (partly dissolved) in freshly distilled ClNP (250 mL), and the mixture was heated, under N_2, with stirring, at 130−135 °C for 22 h. After cooling and filtration, the solid separated was washed with acetone and dried under vacuum (1.3 g). An additional amount of ground material (0.8 g) can be obtained by adding pentane (20% volume) to the mother liquors. The ground material is often contaminated by the presence of $(PcFe)_2N$, easily detectable by visible spectra. Purification can be performed by dissolving fractions of the ground material in THF, followed by filtration and reprecipitation of μ-N by

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† Università di Roma La Sapienza.

‡ ICMAT (CNR).

§ Università di Padova.

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[1] Ercolani, C.; Hewage, S.; Heucher, R.; Rossi, G. *Inorg. Chem.* **1993,** *32,* 2975. Abbreviations used: Pc = phthalocyaninato dianion, $C_{32}H_{16}N_8^{2-}$; TPP = tetraphenylporphyrinato anion, $C_{44}H_{28}N_4^{2-}$; DMSO = dimethyl sulfoxide; ClNP = α-chloronaphthalene; THF = tetrahydrofuran; mim = 1-methylimidazole.

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addition of a nonsolvent (pentane, acetone, or ether) (yield 30–40%). Anal. Calcd for μ-N, $C_{76}H_{44}N_{13}Fe_2$: C, 72.97; H, 3.55; N, 14.56. Found: C, 72.80; H, 3.27; N, 14.32.

(TPP)Fe–N–RuPc (Hereafter Indicated as μ-N′). This complex was prepared by suspending (TPP)FeN_3 (100 mg, 0.14 mmol) partly dissolved) and $(PcRu)_2$ (80 mg, 0.065 mmol) in xylene (10 mL) and heating the mixture at 120 °C for 7 h under N_2, with stirring. After cooling, the solid material was isolated by filtration and washed repeatedly with xylene until the washings were colorless. The solid was then dried under vacuum at room temperature (150 mg, yield 84%). Anal. Calcd for μ-N′, $C_{76}H_{44}FeN_{13}Ru$: C, 70.42; H, 3.42; N, 14.04. Found: C, 69.83; H, 3.43; N, 13.65. Under similar reaction conditions, μ-N′ can be also obtained in ClNP.

Oxidation of μ-N and μ-N′ with I_2. μ-N (100 mg, 0.08 mmol) and I_2 (250 mg, 1 mmol) were added to freshly distilled anhydrous THF (25 mL), and the mixture was allowed to stir at room temperature for 2 days. Addition of heptane (70% volume) determined the precipitation of the oxidized material, which was isolated by filtration, washed with heptane, and dried under vacuum (124 mg, yield 82%). The complex obtained corresponds to the formula [(THF)(TPP)Fe–N–FePc(H_2O)](I_5)·2THF. Anal. Calcd for $C_{88}H_{70}Fe_2I_5N_{13}O_4$: C, 49.86; H, 3.33; N, 8.59; I, 25.47. Found: C, 50.21; H, 3.19; N, 8.40; I, 25.2. (Hereafter this complex will be indicated as [μ-N](I_5)). Recrystallization of the complex can be accomplished from THF–ether, THF–pentane, or acetone–ether. The last mixture was used for the preparation of single crystals suitable for X-ray work. [μ-N′](I_5) was obtained by mixing μ-N′ with I_2 (large excess) in an ampule, which was sealed under vacuum after preliminary N_2–vacuum cycles, and then heating the reaction mixture at 100 °C for 12–14 h. After cooling at room temperature, the ampule was opened and the solid washed with benzene until the washings were colorless. Anal. Calcd for $C_{76}H_{44}FeI_5N_{13}Ru$: C, 47.28; H, 2.30; N, 9.43; I, 32.87. Found: C, 47.44; H, 2.32; N, 9.88; I, 31.99.

Reduction of [μ-N](I_5) and [μ-N′](I_5) with $NaBH_4$. [μ-N](I_5) (50 mg, 0.024 mmol) and $NaBH_4$ (17 mg, 0.5 mmol) were suspended (partly dissolved) in THF (5 mL), and the mixture was stirred at room temperature for 24 h. The solid, isolated by filtration, was washed sequentially with ethanol, H_2O, ethanol, and pentane and dried under vacuum. Examination by IR spectra unequivocally established that the starting precursor μ-N had been formed. A similar procedure was used for [μ-N′](I_5), with identical results.

X-ray Crystal Structure Determination of [μ-N](I_5). (a) Experimental Details. Unit cell dimensions were determined from 25 accurately centered reflections on an Enraf-Nonius CAD4 four-circle diffractometer using a crystal of approximate dimensions 0.25 mm × 0.1 mm × 0.8 mm. Intensity data were collected at room temperature with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) in the θ range 1–25°, covering the index ranges $0 < h < 31$, $0 < k < 13$, $-29 < l < 29$ using the $\omega/2$ scan mode with standard reflections measured at hourly intervals. In all, 7990 reflections were measured, of which 4164 yielded I greater than $3\sigma(I)$. The usual Lp corrections were applied. A plot of the standard reflection showed a 6.4% loss of intensity over the course of the data collection. A decay correction was applied to the observed intensities. ψ-scan data were not obtained for an empirical absorption correction, and efforts to employ the DIFABS program to correct for absorption were unsuccessful, at least in part due to the low data to parameter ratio. Systematic absences occurred for $h0l$ odd, leading to the space groups *C2/c* and *Cc*. On the basis of the fact that there are only four molecules in the cell, combined with the intensity statistics, the noncentrosymmetric space group *Cc* was chosen.

(b) Structure Determination. Using the Patterson method combined with Direct Methods program Multan, it was shown that a V-shaped I_5 group was present, together with two other heavy atom sites identified as the Fe atoms. Normal heavy atom procedures were used to find the remaining atoms of the two macrocyclic molecules. At R = 0.18 a test was carried out on the occupancy factors of the I_5 atom site to check that it was I_5 and not a disordered arrangement of I_3. The occupancy factors indicated that it was I_5.

It was also found that there was an additional atom associated with Fe(2), external to its macrocycle, which, after refinement of occupancy factors, was identified as an oxygen atom of an attached water molecule and not another N atom. With these two points settled, isotropic least-squares refinement converged at R = 0.15.

A difference Fourier map then revealed the presence of three solvent molecules, each consisting of a five-membered ring. These additional molecules were assumed to be THF molecules which had been used as a solvent in the preparation. The atoms of these molecules had very high thermal vibration parameters, resulting in only a very small improvement in R (hydrogen atoms in fixed calculated positions were included in the atom list but were not refined).

Anisotropic refinement was continued on the original uncorrected data, with limited success. By careful choice of weighting scheme

$$w^{-1} = (\sigma(F))^2 + (0.035F)^2 + 3.5$$

and by refining in two parts because of program and computer limitations, R finally converged at 0.062, R_w = 0.076, S = 1.076 with no atoms becoming non-positive definite. The two-stage refinement in the final cycles, on the one hand, was applied to I, Fe, and TPP (N, O, and THF) and, on the other, to I, Fe, and Pc (N, O, and THF fixed). The highest peak in the final difference map was 1.1 electrons.

Other Physical Measurements. IR spectra were recorded on a Perkin-Elmer 983 instrument by using Nujol mulls and CsI windows or by using KBr pellets. 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 contributions of the TPP and Pc ligands were chosen as -386×10^{-6} and 430×10^{-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 Du Pont 950 instrument under a N_2 stream (0.5 L/min). Mössbauer spectral data were obtained as described elsewhere.[9] Elemental analyses for C, H, N, and I (the last determined potentiometrically) were performed by the Servizio di Microanalisi, Area della Ricerca, CNR (Montelibretti).

Results and Discussion

μ-N and [μ-N](I_5). (i) General Remarks. The synthesis of μ-N in ClNP is carried out in anhydrous and deoxygenated atmosphere, so as to avoid the formation of the μ-oxo species ((TPP)Fe)$_2$O or (PcFe)$_2$O, as we already reported for the reaction in xylene.[1] A reaction temperature kept below 150–160 °C prevents the formation of the μ-nitrido dimer ((TPP)Fe)$_2$N.[10] The nearly systematic formation of (PcFe)$_2$N as a contaminant in ClNP is reasonably explained by assuming the N_3^- anion, released by (TPP)FeN_3, to attack PcFe, with formation of PcFeN_3. The latter, in turn, is then thermally decomposed and converted to (PcFe)$_2$N. This μ-nitrido species is practically insoluble in THF, whereas μ-N reaches a solubility of ca. 0.7 mg/mL. This has made possible the separation of the two species, allowing the isolation of pure μ-N (see Experimental Section). The chemical–physical characterization of μ-N has already been given.[1]

[μ-N](I_5) is an air-stable, bluish-black crystalline material, formed by reaction of μ-N with I_2 as a unique material, even using amounts of I_2 lower than that strictly required by its formula. Thermogravimetric analysis shows that [μ-N](I_5) is stable in the range 25–100 °C. At higher temperatures, a continuous weight loss is observed, which makes difficult the interpretation of the nature of the fragments lost (solvent molecules and/or iodine). However, in no case was the spectrum of μ-N reobtained after the thermal treatment, the weight loss

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Table 1. Crystallographic Data for the X-ray Diffraction Study on Crystalline [μ-N](I_5)

chem formula: $C_{88}H_{70}Fe_2I_5N_{13}O_4$	space group = *Cc*
$a = 27.13(1)$ Å	t = room temp
$b = 12.032(5)$ Å	$\lambda = 0.710\,69$ Å
$c = 25.596(41)$ Å	$\varrho_{calc} = 1.697$ g cm^{-3}
$\beta = 90.69(6)°$	$\mu = 22.5$ cm^{-1}
$V = 8298(20)$ Å^3	$R^a = 0.062$
$Z = 4$	$R_w{}^b = 0.076$

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$.

Table 2. Selected Fractional Atomic Coordinates for [μ-N](I_5)

atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)^a
I(1)	0.300	0.3631(2)	0.600	8.46(6)
I(2)	0.32104(7)	0.2202(2)	0.50593(8)	6.42(2)
I(3)	0.3288(1)	0.0844(2)	0.4207(1)	11.64(7)
I(4)	0.23294(8)	0.5226(2)	0.51685(9)	6.89(5)
I(5)	0.17839(8)	0.6494(2)	0.44124(9)	7.41(5)
Fe(1)	0.49858(9)	0.4550(2)	0.2064(1)	1.80(4)
Fe(2)	0.52669(9)	0.2005(2)	0.2450(1)	1.92(4)
O	0.5446(5)	0.040(1)	0.2704(6)	3.5(3)
N	0.5132(6)	0.329(2)	0.2250(7)	2.4(3)
N(11)	0.5962(5)	0.514(1)	0.2223(5)	1.6(3)
N(13)	0.4286(5)	0.418(1)	0.1897(5)	1.5(3)
N(21)	0.5991(5)	0.231(1)	0.2583(6)	2.5(3)
N(22)	0.5218(5)	0.235(1)	0.3188(5)	2.3(3)
O(1)	0.9807(6)	0.122(1)	0.1804(6)	3.8(3)*
O(2)	0.01160(8)	0.421(2)	0.2259(9)	6.4(5)*
O(3)	0.9807(9)	0.419(2)	0.318(1)	7.7(6)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [μ-N](I_5)

I(1)−I(2)	2.991(3)	Fe(2)−N	1.65(2)
I(1)−I(4)	3.259(3)	Fe(2)−O	2.078(13)
I(2)−I(3)	2.829(3)	Fe(2)−N(21)	1.989(14)
I(4)−I(5)	2.756(3)	Fe(2)−N(22)	1.953(14)
Fe(1)−N	1.63(2)	Fe(2)−N(23)	1.904(13)
Fe(1)−O(1)	2.159(40)	Fe(2)−N(24)	1.951(14)
Fe(1)−N(11)	2.037(13)		
Fe(1)−N(12)	2.00(2)		
Fe(1)−N(13)	1.949(12)		
Fe(1)−N(14)	2.02(2)		

I(2)−I(1)−I(4)	88.56(6)	O−Fe(2)−N	179.2(7)
I(1)−I(2)−I(3)	173.3(1)	O−Fe(2)−N(21)	85.8(6)
I(1)−I(4)−I(5)	176.2(1)	O−Fe(2)−N(22)	86.1(6)
N−Fe(1)−N(11)	94.1(7)	O−Fe(2)−N(23)	87.6(6)
N−Fe(1)−N(12)	93.9(8)	O−Fe(2)−N(24)	87.0(6)
N−Fe(1)−N(13)	92.9(7)	N−Fe(2)−N(21)	93.4(7)
N−Fe(1)−N(14)	93.0(8)	N−Fe(2)−N(22)	93.7(7)
N(11)−Fe(1)−N(12)	87.9(6)	N−Fe(2)−N(23)	93.2(7)
N(11)−Fe(1)−N(13)	172.9(6)	N−Fe(2)−N(24)	93.1(7)
N(11)−Fe(1)−N(14)	90.0(6)	N(21)−Fe(2)−N(22)	88.4(6)
N(12)−Fe(1)−N(13)	90.6(6)	N(21)−Fe(2)−N(23)	173.4(6)
N(12)−Fe(1)−N(14)	172.9(6)	N(21)−Fe(2)−N(24)	89.7(6)
N(13)−Fe(1)−N(14)	90.6(6)	N(22)−Fe(2)−N(23)	90.5(6)
Fe(1)−N−Fe(2)	179.0(6)	N(22)−Fe(2)−N(24)	173.0(6)
		N(23)−Fe(2)−N(24)	90.6(6)

probably also implying some decomposition of the material used; no detailed study was made of the residue after the thermal treatment. [μ-N](I_5) is appreciably more soluble in THF or acetone than its nonoxidized precursor; this allowed single crystals for X-ray work to be fairly easily obtained.

It is relevant that the reaction of [μ-N](I_5) with $NaBH_4$ systematically reduces this species to the original μ-N complex, thus showing that the monoelectronic oxidative process can be chemically reversed.

(ii) X-ray Crystal Data and IR, Raman EPR, Mössbauer, and Magnetic Susceptibility Measurements on [μ-N](I_5). The structural and electronic characterization of μ-N as a single-atom-bridged Fe−Fe dimer, previously developed mainly on the basis of analytical, IR, visible, EPR, and Mössbauer data, is given new and strong support by the X-ray structure of [μ-N](I_5) reported here. Summarized crystal data, fractional atomic coordinates, and bond lengths and angles for this salt-like species are given in Tables 1−3, respectively. The structure is shown in Figure 1. The effect of a lack of an accurate absorption correction is evident in the drawing of the molecule, since many of the thermal ellipsoids have unrealistic shapes. The structure shows that the (TPP)Fe and PcFe rings are held together by one briding N atom in a nearly linear Fe(1)−N−Fe(2) bond system (179°) (a side schematic view of the molecule, perpendicular to the Fe−N−Fe axis, is shown in Figure 2). Fe(1) and Fe(2) are practically located in the center of each respective N_4 planar chromopohre, being displaced out of plane, respectively, by only 0.12 and 0.11 Å, toward the bridging N atom.

The two macrocyclic rings are essentially parallel to one another, the angle between the two central N_4 planes being 2.1°, with the only evident out-of-plane locations being the mean planes of the phenyl rings of the TPP ligand which are at angles to the $N_{11}-N_{14}$ plane of 90.5, 98.1, 107.6, and 80.4° for rings C(121)−C(126), C(131)−C(136), C(141)−C(146), and C(151)−C(156), respectively (Figure 1). Minimization of inter-ligand steric repulsions between the two macrocycles, as determined by the phenyl rings of TPP, is obtained by appropriate relative rotation. This drives the two N_4 central systems into an eclipsed position, which, with the exception of the μ-oxo species $(PcAl)_2O$,[11] has never been observed before in X-bridged bimetallic dimers (X = O, N, C) with identical N_4 macrocyclic ligands and central metal atoms.[12]

Both Fe(1) and Fe(2) achieve six-coordination through ligation at the external axial sites of one THF molecule, Fe(1)−O(1) (2.16 Å), and one H_2O molecule, Fe(2)−O (2.078 Å). The hydrogen atoms of the water molecule bound to Fe(2) were never located, but hydrogen bonds occur with O(2) and O(3) of the remaining two THF molecules (O−O(2) = 2.756 Å; O−O(3) = 2.617 Å).

The sandwiched central N atom forms Fe(1)−N and Fe(2)−N bonds of lengths 1.63(2) and 1.65(2) Å, respectively. The slightly longer N−Fe(2) bond on the Pc site is probably due to the stronger trans effect of the coordinated H_2O molecule with respect to that of THF on the TPP site. Comparison of these distances with those observed in structurally related X-bridged dimers shows (Table 4) that they are the shortest observed, although approached closely by those of the complex $[(Br)PcFe]_2N$, and hence in keeping with the presence of strong π-electron delocalization along the Fe−N−Fe bridge. The observed linearity of the Fe(1)−N−Fe(2) bond system, established for other similar single-atom-bridged Fe−Fe dimers

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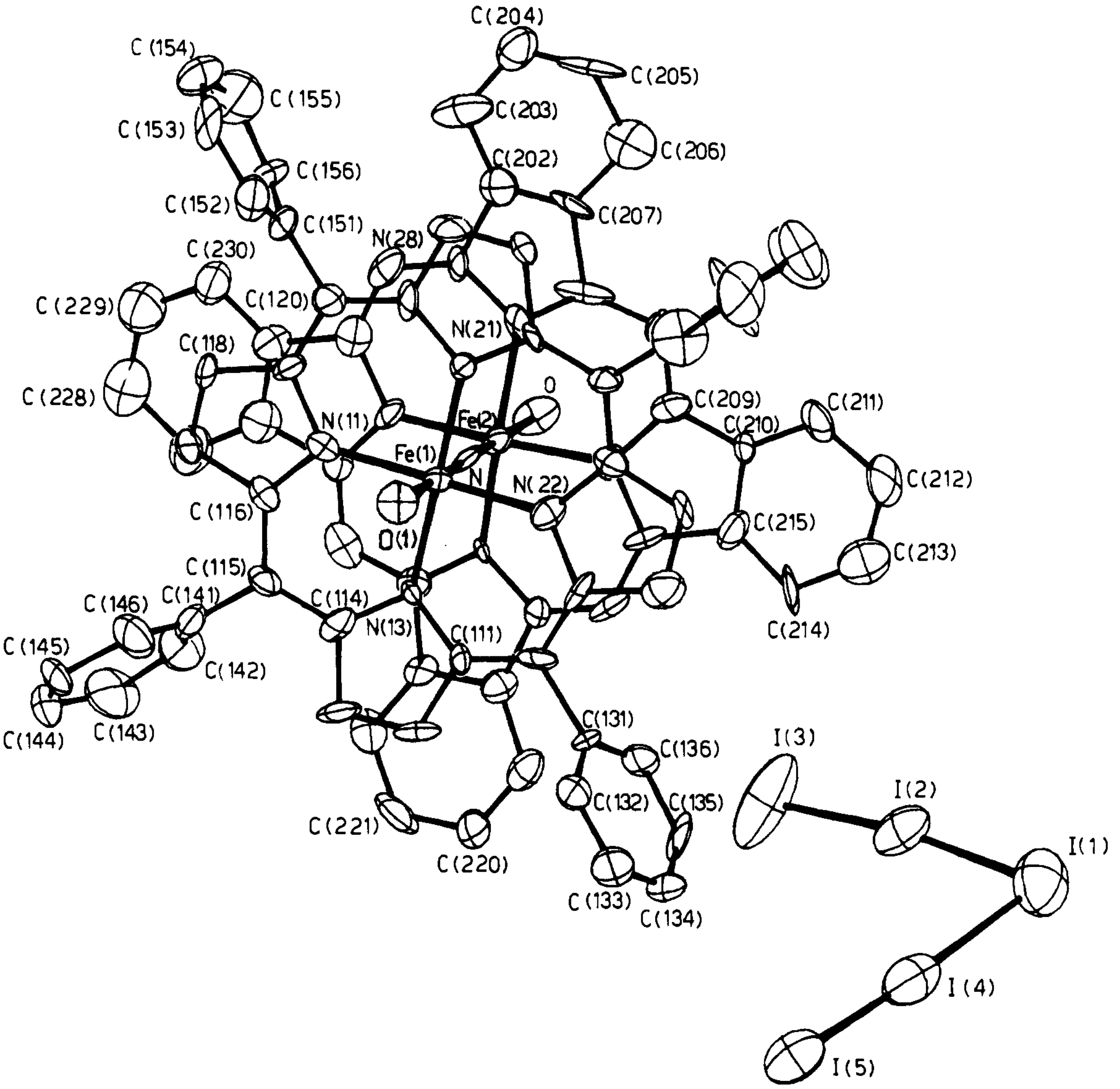

Figure 1. ORTEP view of [μ-N](I_5) showing the labeling scheme adopted (THF molecules neglected).

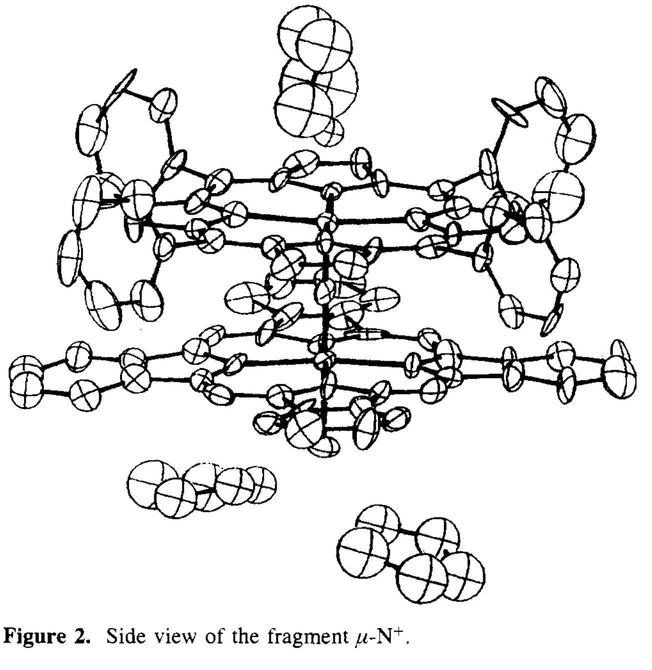

Figure 2. Side view of the fragment μ-N$^+$.

Table 4. Comparison of Structural Data for [μ-N](I_5) and Similar μ-X Species (X = O, N, C)

complex	X_b−M^a (Å)	M−X_a^{b} (Å)	M−N_{eq}^{c} (Å)	M−X−M (deg)	ref
[μ-N](I_5)	1.625(2) (N−Fe(1))	2.078(13) (Fe(2)−O)	1.949(45)	179.0(6)	t.p.^{d}
	1.655(2) (Fe(2)−N)	2.159(40) (Fe(1)−O(1))	2.00(5)		
[(Br)PcFe]$_2$N	1.639(2)	2.495(3)	1.945(6)	180	13
[(mim)PcFe]$_2$O	1.749(1)	2.039(7)	1.92(3)	175.1	14
[(mim)PcFe]$_2$C	1.69(1)	1.95(3)		178(1)	15
[(TPP)Fe)$_2$N]	1.6605(7)	1.991(3)		180.0	16
[(TPP)Fe]$_2$O	1.763(1)		2.087(3)	174.5(1)	17
[(TPP)Fe]$_2$C	1.675			180	18

^{a} X_b = bridging atom (X = N, O, C). ^{b} X_a = external axially ligated X atom (X = O, Br, N). ^{c} Averaged M−N_{eq} bond distances. ^{d} t.p. = this paper.

(Table 4), is certainly attained through the combined action of the π bonding present along the bridge and the close approach (3.28 Å) of the two macrocyclic rings which are forcedly driven to a nearly parallel arrangement.

The uneven V-shaped geometry of the I_5^- group is clearly indicated by the observed internal I−I bond distances, i.e. I(1)−I(2), I(2)−I(3), I(1)−I(4), and I(4)−I(5), found to be 2.991, 2.829, 3.259, and 2.756 Å, respectively. These data indicate that (a) the average bond distance for I(1)−I(2) and I(2)−I(3) is 2.915 Å, quite close to the average bond distance in I_3^-

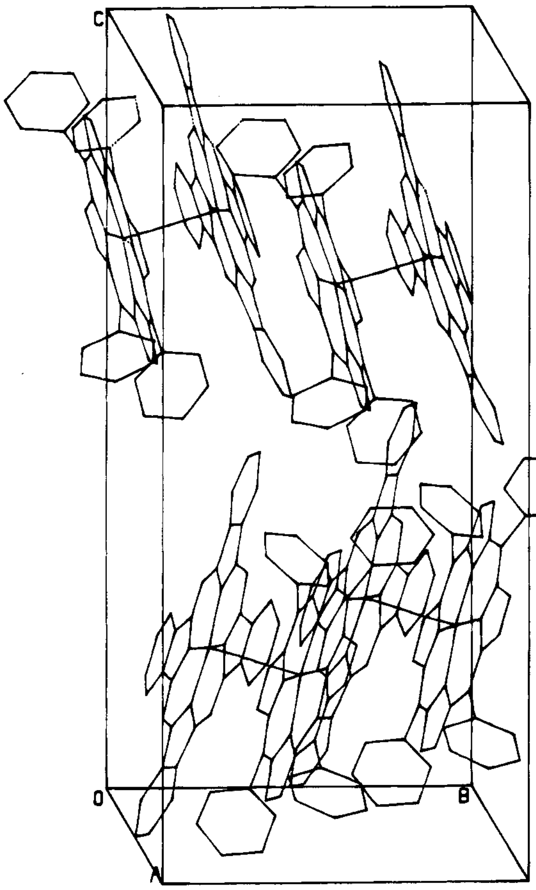

Figure 3. Schematic view of the arrangement of the μ-N$^+$ fragments in the crystal lattice of [μ-N](I_5) (solvent molecules and the I_5^- groups neglected).

(2.920 Å),[19] (b) the bond distance for I(1)−I(4) is quite long, and (c) the bond distance for I(4)−I(5) is very close to that found in crystalline I_2 (2.712 Å).[20] These observations indicate a significant contribution of the (I_3^-)I_2 resonance structure to the electronic structure of the anion. The Raman spectrum of [μ-N](I_5) substantially confirms the presence of the I_5^- group, showing the expected[21,22] absorptions at 165 cm^{-1} (vs) and 140 cm^{-1} (m). The angles at I(2) and I(4) are 173.3 and 176.2°, respectively (Table 3). The angle at I(1) is acute, having a value of 88.56°, below 90°, as found also in a morpholinium pentaiodide (86.9(1)°).[22] The arrangement of the charged fragments μ−N$^+$ in the crystal is shown in Figure 3.

Oxidation of μ-N with I_2 causes the complete disappearance of the very strong IR absorption at 930 cm^{-1}, assigned as ν_{as}(Fe−N−Fe).[1] This is not surprising, since this effect has also been observed in the parallel monoelectronic oxidation reaction of $(PcFe)_2N$.[23] Indeed, this is a useful test for the control of full conversion of μ-N into its oxidized derivative. The presence of the strong ν_{as} absorption is again observed in the IR spectrum of μ-N obtained by reduction of [μ-N](I_5) with $NaBH_4$.

[μ-N](I_5) is EPR silent, excluding the presence of ligand π-cation radicals; hence, oxidation of μ-N must be metal centered. The Mössbauer spectrum of [μ-N](I_5) is given in Figure 4. It shows one clean doublet, indicative of the presence of one type of Fe metal. The isomer shift value (−0.05 mm/s, Table 5), significantly lower than that observed for μ-N (0.113 mm/s), falls in the range observed for several other Fe−Fe single-atom-bridged dimers containing Fe(IV).[12] This definitely indicates the presence of Fe(IV) in [μ-N](I_5).

The room-temperature μ_{eff} value for [μ-N](I_5) is 0.63 μ_B. This low value of the magnetic moment has to be assigned to the presence of small amounts of paramagnetic impurities, fairly commonly observed in phthalocyanine materials, rather than to an intrinsic weak paramagnetism of the bulk material. We have no information at hand to establish whether the diamagnetism of this Fe(IV)−Fe(IV) species (d^4−d^4) is due to the strong antiferromagnetic coupling between the two paramagnetic metal centers via the N atom or, alternatively, to a low-spin ground state ($S = 0$) occurring for each of the two Fe atoms within the dimer.

μ-N′ and [μ-N′](I_5). The synthesis of the heterobimetallic μ-N′ is accomplished by a procedure similar to that described previously for μ-N in xylene.[1] The complex is indefinitely stable to air. Its Mössbauer spectrum is shown in Figure 5, revealing a clean doublet with isomer shift and quadrupole splitting values of 0.03 and 0.90 mm/s, respectively (Table 5). The isomer shift value is significantly lower than those measured for μ−N (0.113 mm/s) and also for $((TPP)Fe)_2N$ (0.16 mm/s) and $(PcFe)_2N$ (0.06 mm/s), all assigned to the presence of Fe(III$^1/_2$), and intermediate between those found for the species $((TPP)Fe)_2C$ (0.10 mm/s) and $(PcFe)_2C$ (−0.16 mm/s), both containing Fe(IV). On this basis, it seems reasonable to suggest the presence of Fe(IV) in μ-N′ and to conclude that the formulation (TPP)Fe^{IV}−N−Ru^{III}Pc is very closely approached. The Fe(IV)−Ru(III) representation can be very likely explained on the basis of the combined action of different ligands and different metal centers. Such formulation implicitly means that the tendency of the two metal ions in the complex to attain a higher oxidation state favors the Fe center.

μ-N′ shows an IR spectrum similar to that of μ-N, with bands of both the TPP and Pc macrocyclic rings, as expected. An absorption of medium intensity, located at 1032 cm^{-1}, is assigned as ν_{as} of the Fe−N−Ru bond system. This value is close to that observed for $(PcRu)_2N$ (1040 cm^{-1}) and the highest if compared with those listed for the related Fe−Fe μ-oxo, μ-nitrido, and μ-carbido dimers containing Pc and TPP ligands (Table 5); this highest position can probably be accounted for if the more localized π electronic charge along the Fe^{IV}=N−Ru^{III} bridge is considered, a fact which should reinforce the antisymmetric stretching vibration of the bond system, with an implied shift to higher frequencies.

The room-temperature μ_{eff} value for μ-N′ is 1.60 μ_B, close to the expected value for one unpaired electron. This suggests

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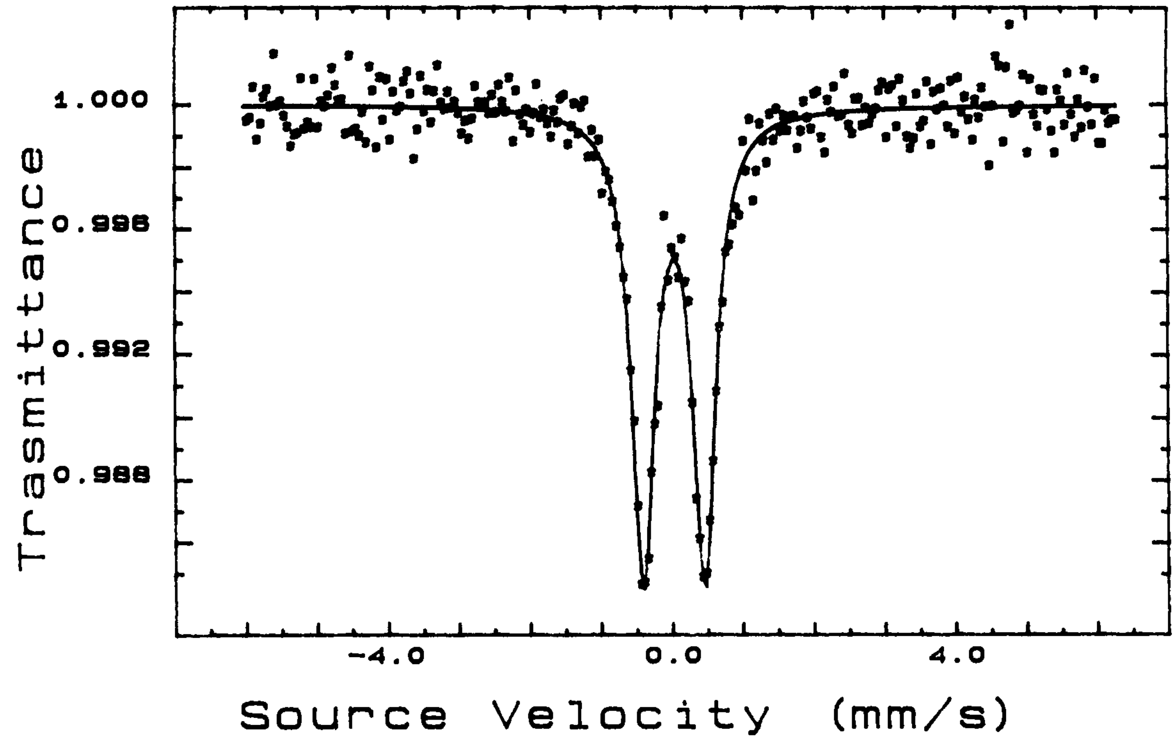

Figure 4. Mössbauer spectrum of [μ-N](I$_5$).

Table 5. IR, Mössbauer, and Magnetic Susceptibility Data for μ-N, μ-N′, [μ-N](I$_5$), [μ-N′](I$_5$), and Related Species

complex	ν_{as} (cm^{-1})	δ (mm/s)[a]	ΔE_Q (mm/s)	Γ (mm/s)[b]	μ_{eff} (μ_B)	ref
μ-N	930 (vs)	0.113	1.467	0.19	2.5−3.0	1
μ-N′	1032 (m−s)	0.03	0.90	0.22	1.60	t.p.[c]
[μ-N](I$_5$)	not obs	−0.05	1.99	0.16	0.63	t.p.
[μ-N′](I$_5$)	not obs	−0.01	1.85	0.23	?	t.p.
[(TPP)Fe]$_2$O	885 m−870 s	0.40	0.62			24
	892 m−878 s					25
(PcFe)$_2$O [μ-Oxo(1)]	852 s−824 s	0.36	0.44	0.16		26
[(TPP)Fe]$_2$N	910 vs−885 m	0.18	1.08			10, 27
(PcFe)$_2$N	915 vs	0.06	1.76	0.19		9, 28
[(TPP)Fe]$_2$C	940 vs−883 sh	0.10	1.88			27−29
(PcFe)$_2$C	990 vs	−0.16	2.69	0.11		30

[a] Referred to the Fe metal. It should be noted that different temperatures (4 K, 77 K, or RT) were used for the registration of the Mössbauer spectra of the listed complexes. Comparison of data is allowed by the fact that different temperatures generally affect only little the observed values. [b] Half-width at half-maximum height. [c] t.p. = this paper.

a low-spin state for the complex, as has been normally found for Fe−Fe couples in similar phthalocyanine and porphyrin complexes.[1] The room-temperature EPR spectrum of μ-N′ shows a low-intensity, narrow (8 G) signal at $g = 2.0017$, certainly attributable to the presence of paramagnetic contaminants.

Treatment of μ-N′ with iodine leads to the monoelectronically oxidized species [μ-N′](I$_5$). The complex is stable to air, poorly crystalline, and much less soluble in THF and acetone than the corresponding Fe−Fe species. Thus no recrystallization was allowed and single crystals suitable for X-ray analysis could not be obtained. Due to the different method of preparation and the consequent absence of any kind of ligated solvent molecules, the complex is not isomorphous with [μ-N](I$_5$); hence, no direct structural relationship with the latter could be established.

The IR spectrum of [μ-N′](I$_5$) is different from that of the starting material only in the complete absence of ν_{as}(Fe−N−Ru) at 1032 cm^{-1}. This band appears again after reaction of the complex with NaBH$_4$. The Raman spectrum of [μ-N′](I$_5$) shows an intense broad double-peaked absorption centered at 165 cm^{-1}, certainly attributable to the I$_5^-$ group.

The Mössbauer spectrum of [μ-N′](I$_5$) definitely indicates the presence of Fe(IV), the isomer shift value being even lower (Table 5) than that observed for the nonoxidized corresponding species. The room-temperature EPR spectrum shows a single, narrow (7 G) signal at $g = 2.0042$. This signal is at least 200 times more intense than that observed for μ-N′, under identical experimental conditions for the spectra and with the use of comparable amounts of samples. In addition, we could verify that the signal has intensity comparable to that evidenced for the π-cation radical present in the species [Pc$_2$Ti](I$_3$)$_{0.66}$.[31] Thus, we are led to suggest that the oxidation of μ-N′ with iodine is ligand centered; the π-cation radical formed should then be formulated as [(TPP)Fe^{IV}=N−Ru^{III}Pc]$^{\bullet+}$. It is intriguing, though, that the IR spectrum gives no evidence supporting such a hypothesis, showing complete absence of signals associated with the phthalocyanine[32] or porphyrin[33] ligand centered oxidation. Room-temperature magnetic susceptibility measurements on various samples of this oxidized material can only roughly

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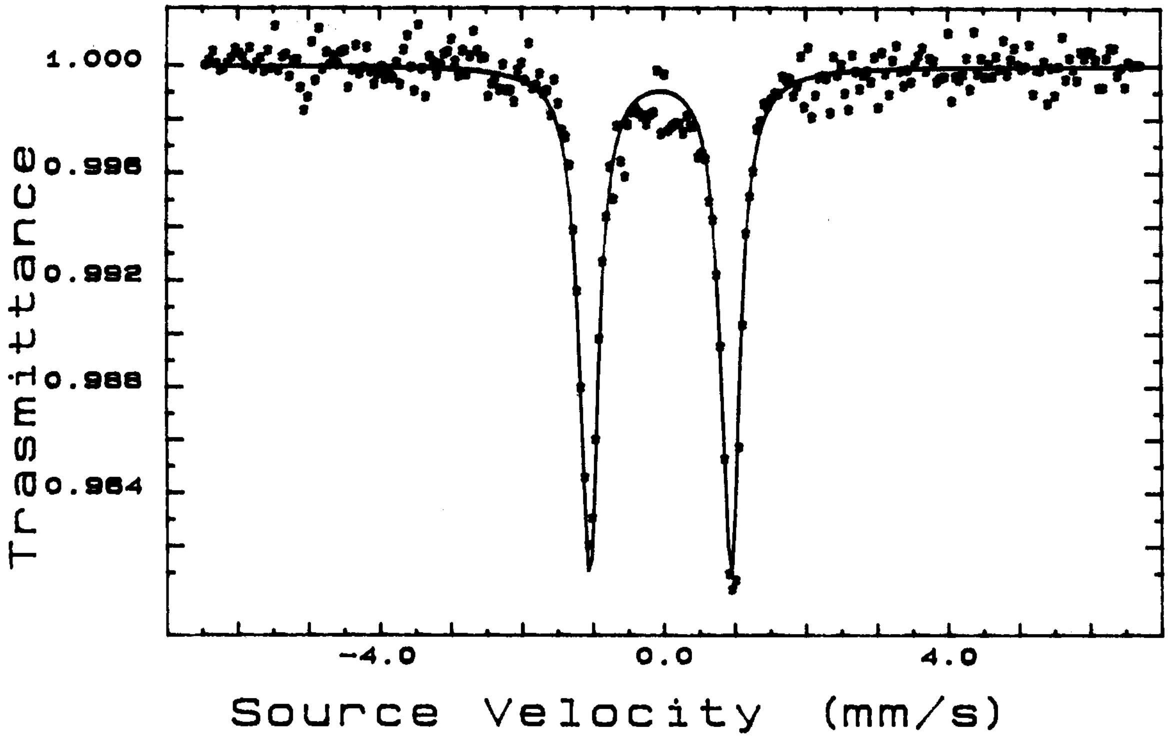

Figure 5. Mössbauer spectrum of μ-N′.

locate μ_{eff} between 1.0 and 2.0 μ_B, thus making unreliable any approach to a further understanding of the detailed electronic structure of this oxidized species.

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Supplementary Material Available: Complete listings of fractional atomic coordinates and isotropic thermal parameters (Table S1), bond lengths and angles (Tables S2 and S3), and general temperature factor expressions (Table S4) (16 pages). Ordering information is given on any current masthead page.

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