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Articles

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High-Valent Iron Phthalocyanine Five- and Six-Coordinated μ-Carbido Dimers

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The μ-carbido dimer $[(PcFe)_2C]$ and its derivatives of formula $[\{(L)PcFe\}_2C]$ (L = acetone, pyridine, 4-methylpyridine, 1-methylimidazole, piperidine) have been prepared and studied by IR, Mössbauer, EPR, and NMR spectroscopy and magnetic susceptibility determinations. All of the complexes appear to contain Fe(IV).

Introduction

We previously extensively described the μ-oxo dimer of formula $[(PcFe)_2O]$,[1] isolated in two different forms (i.e. μ-oxo(1) and μ-oxo(2)) both containing Fe(III),[2] the μ-nitrido dimer $[(PcFe)_2N]$[3] and its monopositively charged derivative $[(PcFe)_2N]^+$,[4] containing Fe(III$^1/_2$) and Fe(IV), respectively, and the two series of N-base adducts of formula $[\{(N\text{-base})PcFe\}_2O]$ (Fe(III))[5] and $[\{(N\text{-base})PcFe\}_2N]^+$ (Fe(IV)) (N-base = py, 4-mepy, pip, 1-meim).[4] We have now extended our attention to the synthesis and characterization of the μ-carbido dimers of formulas $[(PcFe)_2C]$ and $[\{(N\text{-base})PcFe\}_2C]$ (N-base = py, 4-mepy, pip, 1-meim), all shown here to contain Fe(IV).

We previously anticipated some results on $[(PcFe)_2C]$ and its py and 1-meim adducts.[6] After this paper was submitted, we learned of a note[7] on the Mössbauer spectra and magnetism of some (μ-carbido)iron phthalocyanine species, including $[(PcFe)_2C]$ and $[\{(py)PcFe\}_2C]$. As a consequence, the present work, also based on Mössbauer spectral and magnetic susceptibility data, had to be subjected to some revision.

Experimental Section

Preparation of $[(PcFe)_2C]$ (I). As previously outlined,[6] a mixture of PcFe (Eastman Kodak Co.; 300 mg), CI_4 (Aldrich; 500 mg), and sodium dithionite (500 mg) in α-chloronaphthalene (10 mL) was heated in air, with stirring, at 140–150 °C for 30 min. After cooling and filtration, the solid residue was washed with water (to eliminate excess of dithionite) and then with acetone and dried under vacuum (10^{-2} mm) at room temperature for 2 h (200 mg). Anal. Calcd for I, $C_{65}H_{32}N_{16}Fe_2$: C, 67.95; H, 2.8; N, 19.5. Found: C, 67.15; H, 2.8; N, 19.2. Elemental analyses for some samples of I sometimes gave results a little different from those expected, due probably to the presence of some strongly retained solvent (acetone or water) and/or contaminants formed during the reaction. Further purification of I, when necessary, could be obtained by changing the μ-carbido species into a corresponding N-base adduct, followed by elimination of the N-base by heating under vacuum (see below).

I is indefinitely stable to air. It is insoluble in water, ethanol, and common organic nondonor solvents. Thermogravimetric analysis indicates that I is stable at temperatures well above 200 °C, with some loss in weight below 300 °C (1–2%). Infrared spectra of the residue show that I is essentially unchanged after this thermal treatment. X-ray powder spectra indicate that I is not isomorphous with the corresponding μ-nitrido and μ-oxo species (μ-oxo(1) and μ-oxo(2) isomers).

Preparation of the Adducts of Formula $[\{(N\text{-base})PcFe\}_2C]$ (N-base = 4-mepy, py, pip, and 1-meim). Two methods can be used for the preparation of these adducts: (a) dissolution of I in the appropriate N-base, filtration of the solution obtained followed by concentration of the solution in air, and consequent precipitation of the adducts formed; (b) dissolution of I in the N-base, followed by filtration and precipitation of the complex by addition of water (or of an acetone–water mixture).

Methods a and b were successfully used for the py and 4-mepy adducts. Anal. Calcd for $[\{(4\text{-mepy})PcFe\}_2C]$ (VI), $C_{77}H_{46}N_{18}Fe_2$: C, 69.3; H, 3.45; N, 18.85. Found: C, 68.35; H, 3.58; N, 17.95. Anal. Calcd for $[\{(py)PcFe\}_2C]$ (IV), $C_{75}H_{42}N_{18}Fe_2$: C, 68.9; H, 3.2; N, 19.3. Found: C, 68.1; H, 3.25; N, 18.25.

The pip and 1-meim adducts were obtained only by method a. Anal. Calcd for $[\{(pip)PcFe\}_2C]$ (III), $C_{73}H_{44}N_{20}Fe_2$: C, 66.8; H, 3.35; N, 21.3. Found: C, 65.55; H, 3.35; N, 21.25. Anal. Calcd for $[\{(1\text{-meim})PcFe\}_2C]$ (V), $C_{75}H_{54}N_{18}Fe_2$: C, 68.3; H, 4.1; N, 19.1. Found: C, 67.8; H, 4.55; N, 18.7.

Thermogravimetric analyses of the N-base adducts always gave results corresponding to the loss of 2 mol of N-base/mol of adduct, as expected. In all cases the N-base adducts can be converted again into I by heating them at 150–200 °C under vacuum (10^{-2} mm) for 1–2 h.

Physical Measurements. Nujol mull IR, EPR (77 K), and Mössbauer spectra (77 K) and room-temperature magnetic susceptibility measurements of the solid materials were taken as previously described.[4] X-ray powder patterns were obtained with a Debye powder camera (114.6 mm in diameter) with a Cu Kα (Ni-filtered) radiation. Thermogravimetric analyses were performed with a Du Pont 950 analyzer under a stream of N_2 (0.5 L/min). Room-temperture ^1H NMR solution spectra ($CDCl_3$) were obtained with a Bruker WP 200 instrument (operating at 200 MHz) of the NMR Service at the Area della Ricerca di Roma (CNR).

Results and Discussion

$[(PcFe)_2C]$ and Its Acetone Solvate (I and II). $[(PcFe)_2C]$ (I) is a rare species, which, to our knowledge, has only one counterpart in the field of μ-carbido dimers derived from porphyrin or porphyrin-like molecules, i.e. (μ-carbido)bis((5,10,15,20-tetraphenylporphyrinato)iron(III)), $[\{(TPP)Fe\}_2C]$.[8] Most probably these two complexes share structural and electronic similarities. However, I and $[\{(TPP)Fe\}_2C]$ have two quite distinct features: (a) their stability in the presence of N-bases; (b) their tendency

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(1) Abbreviations used in this paper: Pc = phthalocyaninato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion, py = pyridine, 4-mepy = 4-methylpyridine, pip = piperidine, 1-meim = 1-methylimidazole.

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Table I. Mössbauer Spectral Data for $[(PcFe)_2C]$ and Related Species

complex	T, K	δ,[a] mm/s	ΔE_Q, mm/s	Γ,[b] mm/s	%	ref
$[(PcFe)_2O]$ (μ-oxo(1))	77	0.36	0.44	0.16		2, 13
$[(PcFe)_2O]$ (μ-oxo(2))	77	0.26	1.26	0.14		2
$[(PcFe)_2N]$	77	0.06	1.76	0.19		4
$[(PcFe)_2N](PF_6)$	77	−0.10	2.06	0.16		4
$[(PcFe)_2C]$	77	−0.16	2.69	0.11	83	this work
		−0.10	1.49	0.22	15	
		1.48	1.71	0.23	2	
$[(PcFe)_2C]\cdot(CH_3)_2CO$	77	−0.10	1.46	0.15	91	this work
		−0.16	2.60	0.11	6	
		1.16	1.04	0.19	3	
$[\{(4\text{-mepy})PcFe\}_2C]$ (VI)	77	0.03	1.19	0.13	96	this work
		0.12	0.25	0.15	4	
$[\{(py)PcFe\}_2C]$ (IV)	77	0.01	1.16	0.14	90	this work
		−0.05	2.63	0.12	10	
$[\{(pip)PcFe\}_2C]$ (V)	77	0.01	1.11	0.13	100	this work
$[\{(1\text{-meim})PcFe\}_2C]$ (III)	77	0.01	0.94	0.12	100	this work
$[\{(4\text{-mepy})PcFe)\}_2N](PF_6)$	77	−0.10	1.76	0.17		4
$[\{(py)PcFe\}_2N](PF_6)$	77	−0.09	1.76	0.20		4
$[\{(pip)PcFe\}_2N](PF_6)$	77	−0.09	1.73	0.16		4
$[\{(1\text{-meim})PcFe\}_2N](PF_6)$	77	−0.09	1.52	0.13		4
$[\{(4\text{-mepy})PcFe\}_2O]$	4.2	0.20	1.76	0.15		5
$[\{(py)PcFe\}_2O]$	4.2	0.18	1.73	0.15		5
$[\{(pip)PcFe\}_2O]$	4.2	0.19	1.61	0.16		5
$[\{(1\text{-meim})PcFe\}_2O]$	4.2	0.17	1.58	0.14		5

[a] Referred to Fe metal; errors are ±0.01 for the preponderant species and ca. +0.05 for the minor species. [b] Half-width at half-maximum height.

to coordinate donor ligands at the external axial sites of the Fe atoms. As to point a, $[\{(TPP)Fe\}_2C]$ is unstable in a 1 M pyridine solution in benzene,[8a] whereas I is remarkably stable in a solution of pure pyridine, where it can be kept unchanged at room temperature for 24 h or more or even heated at the boiling point temperature without significant degradation of the complex. The stability of I in py compares well with that observed for the corresponding μ-nitrido species $[(PcFe)_2N]$,[3] and is greater than for $[(PcFe)_2O]$, which is easily converted into $PcFe(py)_2$.[2,5] As to point b, no solid adducts have been reported for $[\{(TPP)Fe\}_2C]$; as proved here; instead, interaction of I with the N-bases gives solid stable N-base adducts.

The infrared spectrum of I, examined in the region 4000–600 cm^{-1}, shows an intense absorption centered at ca. 990 cm^{-1}, which can be assigned as ν_{as}(Fe–C–Fe). Contact of I with acetone determines a significant shift of ν_{as}(Fe–C–Fe) to lower frequencies (990 → 940 cm^{-1}), associated with the appearance of a weak band at ca. 1700 cm^{-1} due to ν(CO) of acetone. Shift to lower frequencies of ν_{as}(Fe–C–Fe) is also observed when I is converted into its corresponding N-base adducts of formula $[\{(N\text{-base})PcFe\}_2C]$, with ν_{as}(Fe–C–Fe) at 940 cm^{-1} for $[\{(1\text{-Meim})PcFe\}_2C]$ (III), 910 cm^{-1} for $[\{(py)PcFe\}_2C]$ (IV) and $[\{(pip)PcFe\}_2C]$ (V), and 888 cm^{-1} in the case of $[\{(4\text{-mepy})PcFe\}_2C]$ (VI). Most likely, then, the shift produced by contact of I with acetone, comparable to that observed for III, for which coordination of 1-meim at the metal has been proved by an X-ray study,[6] has to be taken as an indication of axial ligation of the solvent in the acetone solvate II (a similar shift, to 940 cm^{-1}, has also been observed by contact of I with THF).

The low-temperature (77 K) Mössbauer parameters for I and II, together with pertinent data on related systems, are summarized in Table I. Data for I are practically coincident with those published elsewhere.[7] The δ value, which is very close to that found for the isoelectronic μ-nitrido analogue $[(PcFe)_2N]^+$,[4] is strongly indicative of the presence of Fe(IV), as already pointed out.[4] The δ value for II (−0.10 mm/s) is also indicative of the presence of Fe(IV), which means that contact of I with acetone leaves essentially unchanged the oxidation state of the metal.

Remarkably, there is a gradual decrease in the δ value (Table I) in going from the μ-oxo species $[(PcFe)_2O]$ (μ-oxo(1) and μ-oxo(2) isomers) containing Fe(III), through $[(PcFe)_2N]$ which contains Fe(III$^1/_2$), to $[(PcFe)_2N]^+$ and I having Fe(IV), in good agreement with expectation, since δ decreases with increasing the electron density of 4s orbitals, which, in turn, is favored by the loss of 3d electrons. A reverse change, i.e. an increase, is observed for the ΔE_Q values, the ΔE_Q value for I being, to our knowledge, the highest value found among the Fe(IV) derivatives of N_4 macrocycles. This value corresponds to the highest energy value found for ν_{as}(Fe–X–Fe) (990 cm^{-1}) when compared to those of the corresponding μ-nitrido or μ-oxo phthalocyanine species and of the analogous series of the TPP complexes.[6] Thus, the high ΔE_Q value observed for I is likely to be strongly related to the high degree of π-bond conjugation present in the Fe–C–Fe moiety.

N-Base Adducts of $[(PcFe)_2C]$ (III–VI). Two main reasons of interest are associated with the discussion of the molecular and electronic structure of the complexes III–VI. First, six-coordinate μ-carbido dimers have no counterparts in the field of iron tetraphenylporphyrin derivatives, since only the five-coordinate $[\{(TPP)Fe\}_2C]$ has been isolated and characterized.[8] Second, complexes III–VI allow an appropriate comparison with the parallel series of μ-oxo and μ-nitrido species, i.e. $[\{(N\text{-base})PcFe\}_2O]$ and $[\{(N\text{-base})PcFe\}_2N]^+$.[5,4]

Single-crystal X-ray work has been carried out on the species $[\{(1\text{-meim})PcFe\}_2C]$[6] and $[\{(1\text{-meim})PcFe\}_2O]$.[9] Relevant common features evidenced at the molecular level for the two species are as follows: (i) six-coordinate Fe centers having 1-meim ligated at the external axial sites; (ii) a quasi-linear Fe–X–Fe bond system; (iii) a staggered position of the two phthalocyanine rings within the dimer (relative rotation ca. 45°); (iv) eclipsed orientation of the plane of the coordinated 1-meim molecules with respect to the N(Pc)–Fe–N(Pc). We assume that points i–iv apply as well to all the other N-base adducts of I, $[(PcFe)_2N]^+$, and $[(PcFe)_2O]$, neglecting the fact that point iv will not necessarily apply to the pip adducts, since uncertainty exists about the orientation of the (nonplanar) pip molecule. Further structural information, which makes more acceptable the above general assumption, includes the observed isomorphism of the μ-oxo complex $[\{(py)PcFe\}_2O]$[9] with the corresponding manganese μ-oxo dimer $[\{(py)PcMn\}_2O]$, known from X-ray work,[10] for which points i–iv are strictly valid. Isomorphism has also been established between the corresponding two Mn and Fe μ-oxo dimers containing 4-mepy,[4] which extends to this couple of complexes the series for which point i–iv are also valid, since, reasonably, substitution of py by 4-mepy should not change significantly the essential features of the structure.

The Mössbauer data for the complexes III–VI and other pertinent data for the parallel series of μ-oxo and μ-nitrido adducts are summarized in Table I. The following observations can be made as to the isomer-shift values of the complexes III–VI: (a) they fall in the range found for I and II; (b) they are definitely lower than those found for the μ-oxo N-base adducts, containing Fe(III), and approach well those of the μ-nitrido adducts, containing Fe(IV); (c) they vary very little within the series. Points a and b strongly suggest the presence of Fe(IV) in the complexes III–VI. These data fit well with the Mössbauer data just reported on $[(PcFe)_2C]$ and some of its six-coordinate derivatives including IV.[7] We thus conclude that in all the μ-carbido dimers reported here, i.e. I–VI, the presence of Fe(IV) is strongly suggested by the Mössbauer data. In keeping with this, the hypothesis that phthalocyanine π-cation radicals (Pc(−1)) are present in these complexes can be confidently excluded on the basis of IR and EPR data. IR spectra of all the complexes have the expected appearance for the presence of Pc(−2) residues; i.e., they do not show the drastic variations normally associated with phthalocyanine π-cation-radical formation.[11] Low-temperature (77 K) EPR spectra of all of the solid species always indicate the presence of phthalocyanine radicals. However, the low intensity of the signals at high-gain values suggests that the signals are rather due to the presence in the samples examined of minor amounts of radical impurities, as is normal with phthalocyanine materials. Thus, in the complexes under examination, the positive charge is entirely located on the Fe atoms. This suggests that the Fe–C–Fe bond

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system should be adequately represented by the charge distribution Fe(IV)–C(–IV)–Fe(IV), although we reluctantly accept the presence of C(–IV) in the system.

The ΔE_Q values for the complexes III–VI appear to be more sensitive to the nature of the N-base than the δ values and show a decreasing trend that is in remarkable agreement with the sequences observed for the μ-oxo and μ-nitrido analogues (Table I), being also comparable with the total variation within each series. It should also be noticed that the ΔE_Q values measured for the μ-carbido adducts are markedly lower than the value obtained for I and close to the value found for II.

It is particularly significant that the decreasing sequence of the ΔE_Q values, VI (4-mepy) > IV (py) > V (pip) > III (1-meim), is systematically reproduced within each of the other two groups of the μ-nitrido and μ-oxo adducts. We believe that this reproducibility is primarily allowed by the already described structural similarities shared by the three series of complexes and listed in points i–iv. Nevertheless, as the ΔE_Q values depend not only on the electric field gradient generated by the ligands but also on the symmetry of the internal distribution of d electrons at the Fe metal, the spin state and ground state of the latter should also be taken into account for comparison. As regard to the spin state, the following available information has to be considered. (1) The μ-oxo–Fe(III) (d^5) adducts have all been assigned a low-spin configuration mainly on the basis of EPR, Mössbauer, and magnetic susceptibility data.[5] (2) X-ray crystallography on the μ-carbido 1-meim adduct III and its μ-oxo analogue provide average Fe–N(Pc) and Fe–N(1-meim) bond distances close to those of the low-spin Fe(II) (d^6) species [PcFe(N-base)$_2$],[6,9,12] thus suggesting a low-spin state for the mentioned dimers. (3) ^{1}H NMR spectra of III in $CDCl_3$ at room temperature have the typical appearance of essentially diamagnetic systems, with sharp and narrow peaks. (4) Room-temperature magnetic susceptibility measurements on some of the μ-nitrido and μ-carbido adducts gave the following values of the magnetic moment per metal atom: $\mu_{eff} = 1.02\ \mu_B$ for [{(py)PcFe}$_2$N](PF$_6$); 0.99 μ_B for [{(pip)PcFe}$_2$N](PF$_6$); 1.08 μ_B for IV; 0.83 μ_B for III. These low values of the magnetic moment, in combination with the fact that the former μ-nitrido complexes also give ^{1}H NMR spectra suggestive of diamagnetic species, reinforce the hypothesis of low-spin states for these d^4 systems. In summary, then, there seems to be consistent experimental support for the assignment of a low-spin configuration to all the d^5 (Fe(III)) and d^4 (Fe(IV)) N-base adducts under examination.

The definition of the ground state of the present complexes is certainly not facilitated by the low paramagnetism observed and must wait for further information, including magnetic field dependent Mössbauer spectra.

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Electronic Structure and Relative Stability of Isomers of HPX_2, HPXY, and $ClPX_2$ (X, Y = O, S)

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The electronic structure and relative stability of many possible isomers of HPX_2, HPXY, and $ClPX_2$ (X, Y = O, S) are investigated by means of ab initio calculations including polarization functions and electron correlation. For both HPO_2 and HPS_2 series, the three most stable isomers are in the following order: phosphine X═P—X—H (^{1}A′) < phosphorane H—P(X)$_2$ ($^1A_1$) < phosphirane $\mathrm{H{-}\overline{P{-}X{-}X}}$ (^{1}A′) corresponding to relative energies 0, 15, and 105 kcal·mol^{-1} (HPO_2) and 0, 4, and 17 kcal·mol^{-1} (HPS_2). In contrast with HPO_2 series in which only two isomers are found to be stable, for HPS_2 other structures such as (thiosulfinyl)phosphine H—P═S═S (^{1}A′) can be expected as thermodynamically accessible compounds. The substitution of hydrogen by a chlorine atom reverses the thermodynamical ordering, and chlorophosphorane is calculated to be 19.2 and 49.2 kcal·mol^{-1} more stable than the corresponding phosphines for the $ClPS_2$ and $ClPO_2$ series, respectively. This result emphasizes the prominent role of electronic effects of the substituent, which place chlorophosphorane as the most stable structure in agreement with experiment. In the HPOS mixed phosphine, the structural preference is in favor of the thiono form by 7.5 and 4.2 kcal·mol^{-1} for cis and trans conformers, respectively. This result appears to be almost entirely governed by the σ-electronic effects in contrast with the corresponding mixed amines in which the π-effects favored the NO double bond. Finally, vibrational frequencies have been calculated for some low-lying structures and are found to be in excellent agreement with available experimental data.

1. Introduction

Recently, there is increasing interest in the molecular structure and chemical reactivities of compounds involving heavy atoms of group 15 with low coordination number. They are often proposed as reactive intermediates[1] or as ligands to transition-metal fragments.[2]

Although phosphorus and arsenic lie just below nitrogen in the periodic table, it is well-known that their abilities to form multiply bonded compounds are very dissimilar.[3] Among the various possible isomers of the RMX_2 type where M represents an atom of group 15 and X = O, S, Se, only a few of them are experimentally isolated, particularly for phosphorus.

The chemistry of nitrogen is characterized by the important classes of nitro compounds and nitrites whereas the corresponding sulfur analogues are hitherto unknown. Compounds of the type RNS_2 are known to exist as *N*-thiosulfinylamines.[4] Moreover, recently, Nonella, Huber, and Ha[5] succeeded in the preparation of all the possible unbranched isomers of HNSO by energy-se-

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