

## $\mu$ -Carbido-bridged Iron Phthalocyanine Dimers: Synthesis and Characterization

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The synthesis of the  $\mu$ -carbido species of formula  $(\text{pcFe})_2\text{C}$  (pc = phthalocyaninato dianion) has been accomplished by reaction of pcFe with  $\text{Cl}_4$ , while reaction of  $(\text{pcFe})_2\text{C}$  with 1-methylimidazole produces an adduct of formula  $[(1\text{-Meim})\text{pcFe}]_2\text{C}$ ; on the basis of i.r. and visible spectra and single crystal X-ray data, both species have been characterized as  $\mu$ -carbido-bridged Fe dimers.

Following previous studies<sup>1</sup> on the synthesis and description of the molecular and electronic structure of the  $\mu$ -oxo- and  $\mu$ -nitrido-bridged Fe-phthalocyanine dimers of formula  $(\text{pcFe})_2\text{X}$  (X = O, N) [pc = phthalocyaninato dianion,  $(\text{C}_{32}\text{H}_{16}\text{N}_8)^{2-}$ ] we have now extended our attention to the isolation and characterization of the first  $\mu$ -carbido dimer containing a phthalocyaninato ligand, *i.e.*  $(\text{pcFe})_2\text{C}$  (**1**). There is only one previous example of a similar complex in the literature, *i.e.*  $(\text{TPPFe})_2\text{C}$ , containing a tetraphenylporphyrinato ligand dianion (TPP).<sup>2</sup>

The synthesis of (**1**) was accomplished by reaction of pcFe with  $\text{Cl}_4$  in  $\alpha$ -chloronaphthalene in the presence of sodium dithionite, similar to the procedure used for the synthesis of  $(\text{TPPFe})_2\text{C}$ . The mixture was heated at 140–150 °C for 0.5 h, with stirring. After cooling, the reaction mixture was filtered and the solid residue washed ( $\text{Me}_2\text{CO}-\text{H}_2\text{O}$ ) and dried to constant weight under vacuum ( $10^{-2}$  mmHg) at room temperature.

Nujol mull i.r. spectra of (**1**) in the region 4000–600  $\text{cm}^{-1}$  show essentially (a) the disappearance of bands typical for the crystalline  $\beta$ -form (780, 877, 1098 sh, and 1173 sh  $\text{cm}^{-1}$ );<sup>3</sup> (b) appearance of a strong absorption at *ca.* 990  $\text{cm}^{-1}$  of complex structure which is sometimes split clearly with maxima at 989 and 997  $\text{cm}^{-1}$  (form A). In a few cases, a unique intense, sharp absorption with a maximum at 990  $\text{cm}^{-1}$  has been observed (form B). In most cases, however, samples obtained from different preparations give i.r. spectra which appear to be a mixture of forms A and B. The fast atom bombardment (f.a.b.) mass spectra of both forms give the same molecular peak at  $m/z$  1149 (calc. 1148.6).

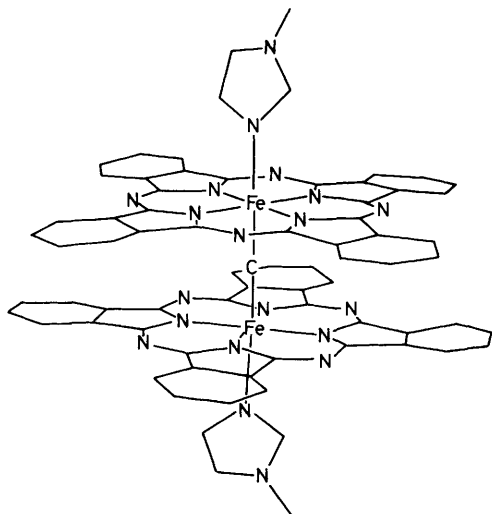


Figure 1. Molecular structure of  $[(1\text{-Meim})\text{pcFe}]_2\text{C}$ .

The new i.r. absorption centered at *ca.* 990  $\text{cm}^{-1}$  for (**1**) can be assigned as  $\nu_{\text{as}}(\text{Fe}-\text{C}-\text{Fe})$ . This absorption is at higher frequency with respect to that found for  $(\text{TPPFe})_2\text{C}$  (940 vs with shoulder at 883  $\text{cm}^{-1}$ ),<sup>2a</sup> indicative of a higher conjugation in the phthalocyaninato complex. This absorption is also at higher frequency with respect to those found for the analogous  $\mu$ -nitrido and  $\mu$ -oxo Fe-phthalocyanine dimers previously studied [ $\nu_{\text{as}}(\text{Fe}-\text{N}-\text{Fe})$  910  $\text{cm}^{-1}$ ; <sup>1b</sup>  $\nu_{\text{as}}(\text{Fe}-\text{O}-\text{Fe})$ , *i.e.*  $\mu$ -oxo (**1**) isomer,<sup>1a</sup> 852 and 824  $\text{cm}^{-1}$ ], as might be expected in view of the higher conjugation capability of the carbon atom with respect to the N and O atoms.

Complex (**1**) is stable to air and has high thermal stability (it can be heated to 280–300 °C in a  $\text{N}_2$  atmosphere without significant decomposition). It is insoluble in water and in most organic non-donor solvents, and slightly soluble in heterocyclic N-bases, such as pyridine and 1-methylimidazole (1-Meim). The visible absorption spectrum in pyridine solution shows an intense band at 620 nm, very close to the position of similar bands observed for  $(\text{pcFe})_2\text{O}$  and  $(\text{pcFe})_2\text{N}$ ,<sup>1</sup> and accompanied by a shoulder of variable intensity depending on the nature of the particular sample examined, at 653 nm. This shoulder is probably owing to the presence of some  $\text{pcFe}(\text{py})_2$  formed by some residual amount of unreacted pcFe always present in the samples of (**1**). The solution spectrum of (**1**) in pyridine is stable for several days at room temperature, while the corresponding  $\mu$ -carbido TPP complex decomposes by 50% in a 1 M pyridine solution.<sup>2a</sup> Furthermore, its stability in pyridine appears to be comparable to that of  $(\text{pcFe})_2\text{N}$  and higher than that of  $(\text{pcFe})_2\text{O}$ , which is instead rapidly converted into the  $\text{Fe}^{\text{II}}$  monomeric bis-adduct,  $\text{pcFe}(\text{py})_2$ .<sup>1a</sup>

Adduct formation with ligation of the N-base at the two Fe atoms of the dimer, only implicitly assumed for (**1**) in pyridine, has been established with 1-Meim. An air stable solid species of formula  $[(1\text{-Meim})\text{pcFe}]_2\text{C}$  (**2**) was obtained by partially evaporating in air a saturated solution of (**1**) in the liquid N-base. Elemental analyses and thermogravimetric measurements for (**2**) confirm the presence of two N-base molecules per dimer. Effective co-ordination of 1-Meim at the Fe atoms of the dimer was proved by (a) a shift of  $\nu(\text{Fe}-\text{C}-\text{Fe})$  from 990 to 940  $\text{cm}^{-1}$  in going from (**1**) to (**2**); (b) the isomorphism of (**2**) with the analogous  $\mu$ -oxo dimer, which has been established<sup>4</sup> as bearing six-co-ordinate low-spin  $\text{Fe}^{\text{III}}$ , with the N-base co-ordinated at the external axial sites of the Fe atoms. Complex (**2**) appears to be the first isolated and well-characterized example of a stable six-co-ordinate  $\mu$ -carbido bridged dimer, since co-ordination of the N-base at  $(\text{TPPFe})_2\text{C}$  has been proposed in solutions of N-bases<sup>2</sup> but stable solid adducts have not yet been isolated.

A partial structure determination of a single crystal containing one molecule of the bis(1-methylimidazole) adduct of the  $\mu$ -carbido dimer, one molecule of the bis(1-methylimidazole) adduct of  $\text{Fe}^{\text{II}}(\text{pc})$ , and three molecules of acetone solvate was

performed.† A view of the  $\mu$ -carbido dimer portion of the structure is shown in Figure 1. Despite the poor quality of the structure, some definite conclusions can be drawn: (i) the  $\mu$ -carbido dimer structure has been clearly identified; (ii) the Fe centre is clearly six-co-ordinate, bound to the bridging carbon atom, the four pc nitrogen atoms, with a 1-Meim

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† *Crystal data* for complex (2):  $[\text{Fe}(\text{pc})(1\text{-Meim})]_2\text{C}\cdot\text{Fe}(\text{pc})(1\text{-Meim})_2\cdot 3\text{-Me}_2\text{CO}$  (only crystals obtainable),  $M = 2229.55$ , monoclinic, space group  $C2/c$ ,  $a = 35.309(9)$ ,  $b = 14.503(15)$ ,  $c = 23.161(12)$  Å,  $\beta = 103.81(13)^\circ$ ,  $U = 11,517$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.28$  g cm<sup>-3</sup>. 5850 Unique reflections were obtained using Mo- $K_\alpha$  radiation on an Enraf-Nonius CAD-4 diffractometer and refined using least-squares methods to  $R = 20.1$ ,  $R_w = 17.1$ . Despite apparent good crystal quality as judged by visual examination, all crystals diffracted poorly. The diffracted peaks were unacceptably broad with some intense peaks overlapping, the intensities diminished rapidly as a function of  $2\theta$  such that no observable reflections were observed above  $2\theta = 40^\circ$ . Significant decomposition of the crystal in the X-ray beam also occurred. This was partially corrected during the data reduction process. Yet, because of the inherent interest of the  $\mu$ -carbido structure, a data set was collected and the structure solved to confirm our other findings. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

occupying the sixth co-ordination site; (iii) the two phthalocyanine rings are rotated approximately  $45^\circ$  relative to one another. (iv) Less accurately determined are the Fe-C bond distance, 1.70(1) Å, Fe-C-Fe angle,  $178(1)^\circ$ , Fe-N(pc) distance, 1.92(2) Å, and Fe-1-Meim distance, 2.06(2) Å.

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