Nitrido-bridged Iron Phthalocyanine Dimers: Synthesis and Characterization

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A new macrocyclic N-bridged species of formula [PcFe–N–FePc] (Pc = phthalocyaninato anion, $C_{32}H_{16}N_8{}^{2-}$) has been prepared by reaction of PcFe with NaN_3 in α-chloronaphthalene and structurally and electronically characterized by i.r., visible, *X*-ray powder, and e.s.r. measurements: one-electron oxidation leads to the cationic species $[PcFe–N–FePc]^+$, which has been isolated as the $PF_6{}^-$ salt.

Nitrido-bridged metal complexes are rare and $[TPPFe]_2N$ (TPP = 5,10,15,20-tetraphenylporphinato anion) is the only well characterized N-bonded species of this type containing a first row transition metal.[1] Even though $[TPPFe]_2N$ has been extensively studied,[2] questions remain as to the details of the bonding.[3] Accordingly, other examples are needed to test the validity of our current understanding and to ascertain the generality and conditions under which nitrido-bridges can be stabilized. We report that phthalocyaninatoiron(II), PcFe, also forms a stable nitrido dimer, *i.e.* [PcFe–N–FePc] (L), which readily undergoes a one-electron oxidation to form a stable cation, L^+. Aside from analytical data, the characterization as an N-bridged dimer is shown unequivocally from a comparison of *X*-ray powder patterns, e.s.r. and i.r. spectra with those of closely related analogues.

Although PcFe does not form a stable Fe^{III} azide complex, heating PcFe in boiling α-chloronaphthalene with NaN_3 results in rapid thermal decomposition of the azide and the formation of L. Of particular significance is that under these conditions the μ-oxo complex, $[PcFe]_2O$, recently reported,[4] also reacts with azide yielding the same nitrido-bridging complex, thus eliminating the μ-oxo complex as the most likely impurity. L is highly insoluble, except in moderately strong donor solvents such as n-butylamine, 1,3-diaminopropane, or pyridine. It is stable in solution towards dissociation or disproportionation and in this sense its behaviour is markedly different from that shown by the corresponding μ-oxo-Fe^{III} derivative which is much more easily reconverted into the Fe^{II} species $[PcFe(py)_2]$ in the presence of pyridine.[4] L is paramagnetic with one unpaired electron per dimer unit and shows a typical axially symmetric e.s.r. spectrum in N-donor bases at liquid N_2 temperature ($g_{\parallel} = 2.03, g_{\perp} = 2.13$), consistent with an A_1 ground state and indicative of extensive charge delocalization over the two iron centres with little N(p) character, similar to that of $(TPPFe)_2N$.[5] L is isomorphous with the crystalline form of $[PcFe]_2O$, presumed to have a linear Fe–O–Fe moiety [*i.e.* μ-oxo(2)[4]]. L also shows a visible spectrum in pyridine with a strong band at 625 nm in the same region as that observed for $[PcFe]_2O$. Its i.r. Nujol mull spectrum exhibits a very intense absorption, tentatively assigned to the antisymmetric Fe–N–Fe stretch, at 915 cm^{-1}, very close to that found for $[TPPFe]_2N$ (910vs and 885m cm^{-1}).[1]

The complex is oxidized to a cationic species with moderately strong oxidants such as tetracyanoquinodimethane or the ferricinium cation in CH_2Cl_2 and can be crystallized from pyridine–CH_2Cl_2 solution as the $PF_6{}^-$ salt, $[L(py)_2]PF_6$. This dimagnetic salt is also stable in solution and its ^1H n.m.r. in CD_2Cl_2–($^2H_5$)pyridine shows Pc benzenoid resonances at δ 8.47 and 9.10. Oxidation of the neutral species to the cationic species is accompanied by a bathochromic shift of the absorption maximum to 635 nm; reduction with $BH_4{}^-$ regenerates the initial product. Interconversion of oxidation states was monitored by the changes in the visible spectrum, as well as characterization of the solid products.

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