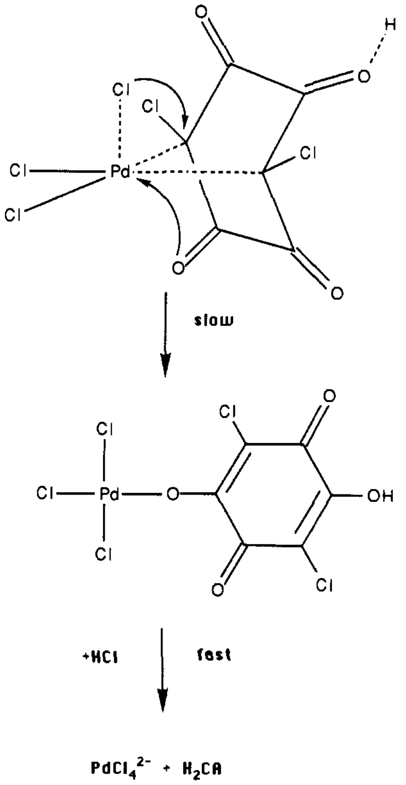

Figure 4. Proposed mechanism of the k_2 pathway for displacement of carbon-bonded chloranilate from $[Pd(C\text{-}CA)Cl_2]^{2-}$ by hydrochloric acid.

reactions, rate law 2 may result from concerted electrophilic and nucleophilic attacks by H^+ and Cl^- on the Pt–C bond or alternatively from the intermediacy of a Pt(IV) complex generated by oxidative addition of HCl; RH would then follow from a rapid reductive elimination process.[21]

Considering the rarity of Pd(IV)–alkyl complexes,[22,23] the documentation of oxidative-addition processes for Pd(0) but not Pd(II),[24] and the lack of a precedent for a Pd(IV)–hydride species, it is extremely unlikely that the k_2 pathway for protonolysis of $[Pd(C\text{-}CA)Cl_2]^{2-}$ reflects oxidative addition of HCl in the rate-determining step. A more straightforward mechanistic hypothesis (Figure 4) invokes rate-limiting Pd–C bond breaking facilitated by the attack of an axially bound nucleophile, coupled with protonation of a carbonyl oxygen atom to promote its conversion to a phenolic –OH group as $C\text{-}CA^{2-}$ is transformed into the *p*-quinone form of HCA^-. On this basis, the k_1 pathway is readily understood in terms of H_2O replacing Cl^- as the activating nucleophile; taking $[H_2O]$ as ca. 55.5 M, the third-order rate constant corresponding to H_2O-assisted chloranilate protonolysis (k_1') is calculated to be 5×10^{-5} M^{-2} s^{-1} and $k_2(Cl^-)/k_1'(H_2O) = 4 \times 10^2$, in accord with the expected reactivity advantage for the softer nucleophile. Although the proposed $PdCl_3(HCA)^{2-}$ intermediate appears reasonable, rate-determining proton attack at a Pd–C bond, resulting in the immediate release of chloranilate from the first coordination sphere of palladium, cannot be ruled out.

The present findings on the displacement of carbon-bonded chloranilate provide an interesting contrast to mechanistic studies of $Pd(acac)_2$ protonolysis in hydrochloric acid, yielding $Pd(acac)Cl_2^-$ and Hacac products.[25] In the case of acac displacement from $Pd(acac)_2$ at constant $[H^+]$, a two-term rate expression of the form $k_{obsd} = k' + k''[Cl^-]$ pertains, in agreement with our results on $[Pd(C\text{-}CA)Cl_2]^{2-}$, but k_{obsd} approaches a saturation limit with increasing $[H^+]$ instead of following a simple first-order dependence. Pearson and Johnson attribute this saturation behavior to the protonation of a monodentate acetylacetonate moiety generated by chloride ion induced ring opening.[25] Such protonation evidently retards reclosure of the acac chelate ring, promoting the second Pd–O bond cleavage reaction that leads to $Pd(acac)Cl_2^-$ and free Hacac. The first-order hydrogen ion dependence of reaction 1 rules out the formation of a half-opened chloranilate chelate species analogous to [Pd(acac)(acacH)Cl] in the protonolysis pathway but is entirely consistent with the partial protonation of a weakly basic carbonyl group of the $C\text{-}CA^{2-}$ ligand.

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-735) is gratefully acknowledged.

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Contribution from the Department of Chemistry, Monash
University, Clayton, Victoria 3168, Australia,
and Institute of Inorganic Chemistry, University of Kiel,
Olshausenstrasse 40, 2300 Kiel 1, West Germany

Iron(IV) Phthalocyanines. Mössbauer Spectral Studies of (μ-Carbido)(phthalocyaninato)iron(IV) and of Its Axially Ligated and Oxidized ($Pc^{\bullet+}$ π Cation Radical) Derivatives

Eddy N. Bakshi,[†] Christopher D. Delfs,[†] Keith S. Murray,*[,†]
Birgit Peters,[‡] and Heiner Homborg*[,‡]

Received June 1, 1988

We have recently described the electronic features of μ-bridged iron phthalocyanine complexes of type $(FePc)_2X$, where X = O^{2-} or N^{3-}, and showed that Mössbauer spectroscopy was a particularly useful technique for assigning formal oxidation states and spin states to iron in these compounds.[1-5] In the μ-oxo compounds the isomer shift (δ) and quadrupole splitting (ΔE_Q) were indicative of $S = {}^5/_2$ Fe(III) centers in both of the crystalline isomers μ-oxo(**1**) and μ-oxo(**2**), and it was possible to distinguish different geometric features in the two isomers from differences in the size of ΔE_Q.[1,2] Some novel six-coordinate Lewis-base adducts of type $(LFePc)_2O$, where L = pyridine, imidazole, etc., were assigned as low-spin ($S = {}^1/_2$) Fe(III) centers from consideration of the Mössbauer and magnetic susceptibility data.[3] The δ value for the μ-nitrido complex $(FePc)_2N$ was observed to be close to zero and thereby indicative of considerable iron(IV) character.[4,5] We now describe the Mössbauer features of the μ-carbido complex $(FePc)_2C$ and of a range of its six-coordinate Lewis-base adducts and oxidized derivatives. Carbido complexes of transition metals are still generally not widely established. The porphyrin analogue $(FeTPP)_2C$ is one notable example of this interesting class of compounds, and its Mössbauer parameters are included here for comparison.[6-8] A well-established set of Mössbauer parameters for Fe^{IV} macrocycles, especially those containing the Pc(1−) cation radical ligand, are also useful for comparison with the values reported for Fe^{IV}-heme proteins such as peroxidases.[7,8]

The syntheses and spectral and structural features of the present compounds will be described in detail elsewhere. While the present paper was being written, a short note on the synthesis and preliminary structural features of $(FePc)_2C$ was published by Rossi et al.,[9] but no data on Mössbauer spectra or magnetic moments were reported.

Experimental Section

The syntheses and properties of the complexes are described in detail elsewhere.[10]

Mössbauer spectral measurements and line-shape-fitting routines were carried out as described previously.[1-4] Isomer shifts are quoted relative to α-Fe.

[†] Monash University.

[‡] University of Kiel.

Table I. Mössbauer Parameters for μ-Carbido FePc Complexes and Related Systems at 77 K[a]

no.	complex	δ, mm s^{-1}	ΔE_Q, mm s^{-1}	hwhm, mm s^{-1}	ref
	Five-Coordinate Fe^{IV}Pc(2−)				
1	(FePc(2−))$_2$C	−0.04	2.67	0.16	tw
2	(FeTPP(2−))$_2$C	0.10[b]	1.88		8
3	(FeTPP(2−))CCl$_2$	0.10[b]	2.28		8
4	[FePc(2−))$_2$N]I$_3$	−0.11	1.98	0.14	21
	Six-Coordinate Fe^{IV}Pc(2−) Containing Neutral and Anionic Axial Ligands				
5	[(pyFePc(2−))$_2$C]·0.5py	0.01	1.14	0.15	tw
6	[(thf)FePc(2−))$_2$C]thf	0.00	1.84	0.16	tw
7	[(pyFePc(2−)]$_2$N]I$_3$	−0.11	1.86	0.17	21
8	(TBA)$_2$[(FFePc(2−))$_2$C]·5H$_2$O	0.01	1.14	0.21, 0.22[c]	tw
9	(TBA)$_2$[((CN)FePc(2−))$_2$C]·2.5CH$_2$Cl$_2$	0.01	0.22	0.17	tw
10	(TBA)$_2$[((OCN)FePc(2−))$_2$C]·2H$_2$O	0.03	0.78	0.16 (40.3%)	tw
		0.03	1.17	0.20 (59.7%)	
11	(TBA)$_2$[((SCN)FePc(2−))$_2$C]·2H$_2$O	0.03	1.18	0.18	tw
	Six-Coordinate Fe^{IV}Pc(1−) Containing the Radical Cation Pc(1−) Group				
12	[(ClFePc(1−))$_2$C]Cl$_{1.5}$·CH$_2$Cl$_2$	0.00	1.16	0.22	tw
13	[(BrFePc(1−))$_2$C]Br$_4$·0.5EtOH	0.00	1.65	0.23	tw
14	[((NO$_3$)FePc(1−))$_2$C]·2H$_2$O	0.01	1.28	0.23	tw
	Iron(IV)-Heme Enzymes				
15	HRP(I)	0.08	1.25		14b
16	HRP(II)	0.03	1.61		14a
17	CytC-P(ES)	0.05	1.55		22
18	chloroP(I)	0.15	1.02		23

[a] Abbreviations: TPP^{2-} = tetraphenylporphyrin dianion, TBA$^+$ = tetrabutylammonium, py = pyridine, thf = tetrahydrofuran, HRP = horseradish peroxidase, cytC-P(ES) = cytochrome C peroxidase enzyme substrate complex (H$_2$O$_2$ oxidation of cyt-C-P), chloroP = chloroperoxidase, hwhm = half-width at half-maximum height, tw = this work. [b] Measured at 131 K. [c] Fitted to two singlets.

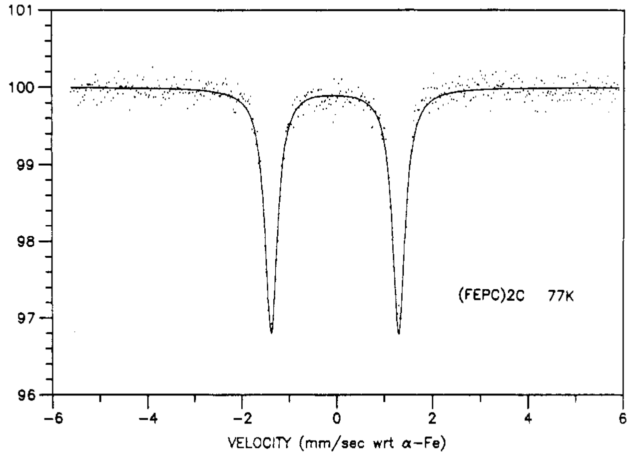

Figure 1. Mössbauer spectrum of (FePc(2−))$_2$C (**1**) at 77 K.

Results and Discussion

The Mössbauer spectrum of a representative example of this μ-carbido iron phthalocyanine series is shown in Figure 1. A sharp, well-detailed doublet is indicative of the presence of only one iron environment. The isomer shift and quadrupole splitting values for all of the compounds are given in Table I. The most notable general feature is that the isomer shift values are close to zero or are slightly negative. This is indicative of reduced s-electron density at the Fe nuclei and compatible with Fe being in the +IV oxidation state. The δ values are more negative than in the porphyrin analogues **2** and **3**[8] although a similar value has been noted for a monomeric dimethoxoiron(IV) porphyrin complex.[11] Negative isomer shifts were also observed for the isoelectronic μ-nitridoiron(IV) phthalocyanine complexes **4** and **7** (Table I). It is interesting to note that neither axial ligation, as in **5–10**, nor oxidation of the Pc(2−) ligand to the cation radical Pc(1−), as in **12–14**, influences the magnitude of δ in any significant way except perhaps for very small shifts to more positive values. This suggests that the carbido group primarily determines the distribution of electron density at the metal nuclei.

There are some interesting features in the relative sizes of the quadrupole splitting, ΔE_Q. First, the parent μ-carbido complex, **1**, displays the largest splitting in the present series and in all known iron(IV) phthalocyanine and porphyrin compounds. The size of ΔE_Q reflects the nature of the ligand field presented at Fe by the five-coordinate C–FePc core as well as the precise electron occupancy, i.e. spin state. It is not possible to definitely assign the Fe(IV) spin states until applied-field Mössbauer studies are carried out. Magnetic susceptibility data do not, unfortunately, clarify the spin state. Because of the strong antiferromagnetic coupling across the Fe$_2$C bridge, the complexes are close to being diamagnetic.[12] Complex **1**, for instance, shows $\mu_{Fe} = 0.9\ \mu_B$ at room temperature.[24] Coordination of a sixth ligand, in the form of a neutral Lewis-base (**5** and **6**) or anionic ligand (**8–10**) generally leads to a decrease in the size of ΔE_Q. The cyano complex, **9**, shows a very small splitting, similar in magnitude to that of the structurally characterized monomeric dicyanoiron(III) complex, **1b**.[13] This small splitting presumably results from the effect of two C-bonded ligands (formally CN$^-$ and C^{4-}) disposed trans

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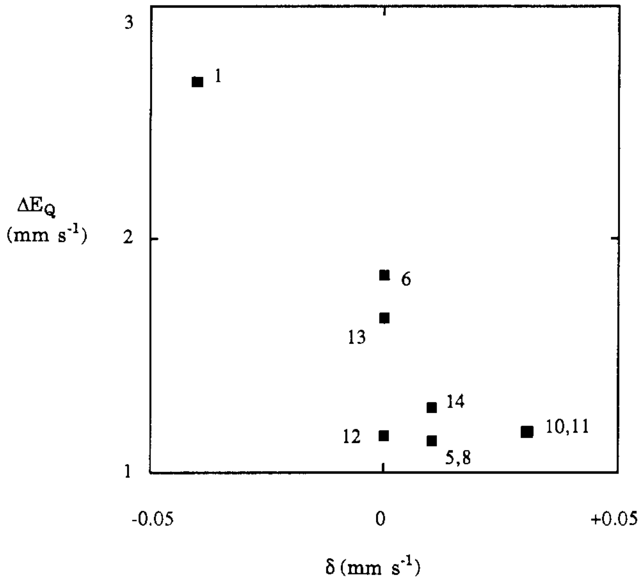

Figure 2. Plot of isomer shift vs quadrupole splitting at 77 K for μ-carbido iron(IV) phthalocyanine complexes.

to each other about each Fe^{IV}Pc macrocyclic moiety. The precise ordering and separations of the single-ion energy levels appropriate to a [(CN)Fe^{IV}(Pc)C] fragment are very difficult to obtain experimentally but are likely to be different from those generated by fragments such as [pyFe^{IV}(Pc)C], [(thf)Fe^{IV}(Pc)C], and [FFe^{IV}(Pc)C] found in **5**, **6**, and **8**.

One of the interesting observations to emerge from the present δ and ΔE_Q values is their close similarity to those determined for the Fe^{IV} forms of iron proteins such as horseradish peroxidase, chloroperoxidase, etc. (**15–18**).[7,8,11,14,15] It is now reasonably well established[16] that compounds I and II of these proteins contain oxoiron(IV) porphyrin centers of the kinds OFe^{IV}(P$^{\bullet+}$) and OFe^{IV}(P), respectively, each bonded to the protein via a sixth axial "ligand".[7,8,11] P$^{\bullet+}$ represents the π cation radical form of the heme group, the same oxidation level as that found in the present Pc(1−) complexes **12–14**. There are a small number of synthetic model porphyrin–Fe^{IV} compounds available to compare with these high-valent iron enzymes, the best known being the complexes [OFe^{IV}(TPP)(*N*-Meimd)][17,18] and [(MeO)$_2$Fe^{IV}(TMP)],[11] which contain the normal dinegatively charged porphyrin ligand, and [OFe^{IV}(TMP$^{\bullet+}$)], which contains the π cation radical form of the sterically hindered tetramesitylporphyrin ligand.[19] Binuclear μ-nitrido and μ-carbido iron(IV) porphyrins have also been studied in some detail.[8,20]

The IR and visible spectra and the electrochemical properties of complexes **12–14** clearly show that they contain the Pc(1−) (i.e. (Pc$^{\bullet+}$)) π cation radical form of the phthalocyanine ligand.[10] Further confirmation of ligand-centered oxidation is evident in the Mössbauer data in Table I, where it can be seen that the δ and ΔE_Q values are very similar to those of the Fe^{IV}Pc(2−) species.

Lang et al. have recently shown, by means of applied-field Mössbauer studies and a crystal-field ($S = 1$ spin Hamiltonian) model for the low-spin Fe^{IV} centers in the heme enzymes and porphyrin models, that a rather uniform relationship between δ and ΔE_Q values exists.[11,19] This, in turn, was proposed to be related to differences in d$_{z^2}$-bonding electron density (where z is the Fe═O direction). The present zero-field Mössbauer data generally seem to fit into this interpretation although a plot of δ vs ΔE_Q, while reasonably linear (Figure 2), shows a steeper slope than does the analogous iron porphyrin plot presented in ref 11b. This may be a result of comparing OFe(porph)L with CFe(Pc)L. The values for **1**, for instance, would suggest that the Fe^{IV}(Pc(2−))C core produces very small d$_{z^2}$-bonding density and the electric field gradient at Fe arises essentially from contributions by the valence electrons alone.[11] The other axially ligated complexes show increased d$_{z^2}$-bonding electron density. The cyano complex, **9**, does not fit this model, possibly because of CN$^-$ π-bonding effects and/or a markedly different overall crystal-field splitting, alluded to earlier.

Acknowledgment. We wish to thank Associate Professor J. D. Cashion (Department of Physics, Monash University) for access to Mössbauer facilities and fitting programs. K.S.M. acknowledges financial support from the Australian Research Grants Scheme and Monash University Special Research Grants.

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(24) A reviewer suggested that some of the Fe^{IV}Pc fragments in these binuclear species might have spin-paired, $S = 0$, spin states. While this is possible, it is unlikely in view of the $S = 1$ states displayed by Fe(IV) porphyrins and the nonzero μ_{Fe} values observed. Ongoing applied-field Mössbauer and variable-temperature susceptibility studies should help clarify matters.

Contribution from the Laboratorium voor Radiochemie,
K. U. Leuven, Celestijnenlaan 200G, B-3030 Heverlee, Belgium

Electrochemical Oxidation of Ruthenium(IV) at Platinum Rotating Disk Electrodes: Preparation and Characterization of a Tetrameric Ruthenium(4.25) Species

L. Heerman,* H. Van Nijen, and W. D'Olieslager

Received May 27, 1987

Ruthenium(IV) exists in noncomplexing acid media, e.g. perchloric acid solutions, as a tetrameric ion formulated as Ru$_4$(OH)$_{12}$$^{4+}$.[1,2] The evidence for the existence of this species and its redox chemistry have been reviewed recently.[3] The electrochemical reduction of Ru$_4$(OH)$_{12}$$^{4+}$ on noble metal electrodes[1,4] and mercury electrodes[5,6] has been investigated in detail and is now fairly well understood. However, much less work has been performed on the anodic oxidation of ruthenium(IV), despite the fact that several literature reports suggest the existence of a ruthenium(4.25) species.[7-11] Wehner and Hindman[7] observed

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