^1H NMR (cf. supplementary Material).

The molecular structure of the $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2]^{3+}$ cation (Figure 1) consists of two *cis*-$(NH_3)_2Pt(III)$ units bridged by two 1-MeU ligands head-to-head, with Pt1 (coordinated to the two 04′ oxygens) carrying a nitro group in the axial position. Counting each Pt as one ligand for the second Pt, Pt1 has the coordination number 6, while Pt2 has 5 only. The Pt-Pt distance is 2.607 (1) Å, the Pt1-*N*O_2 distance is 2.06 (2) Å. Pt-NH_3 (2.03 (1)-2.07 (2) Å), Pt-N3 (2.02 (2) Å), and Pt-O4′ distances (2.01 (1), 2.04 (1) Å) are normal, as is the geometry of the nitro ligand (N–O 1.20 (2) Å, av O10–N12–O11 122 (2)°). The two Pt planes are tilted by 19° but almost eclipsed (twist angle about the Pt–Pt vector 3.6°, av).

Intermolecular hydrogen bonding involves NH_3 groups and nitrate oxygens, O11 of the NO_2 group and NH_3, NH_3 and lattice water, and lattice water and O2a′. None of these interactions are unusually short (≥2.74 Å), and there are no long-range Pt–Pt interactions (shortest intermolecular distance 6.3 Å).

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Supplementary Material Available: Atomic positional and thermal parameter and ^1H NMR data (2 pages). Ordering information is given on any current masthead page.

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(15) Anal. Calcd for $[(NO_2)(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2](NO_3)_3\cdot H_2O$: C, 12.53; H, 2.53; N, 17.54; O, 26.70. Found: C, 12.61; H, 2.49; N, 17.69; O, 26.35.

(16) X-ray analysis: Space group $C2/c$, $a = 19.257$ (5) Å, $b = 17.611$ (5) Å, $c = 15.389$ (2) Å, $\beta = 109.44$ (2)°, $V = 4924.2$ Å^3, $Z = 8$, ρ_{obsd} 2.55 g cm^{-3}, ρ_{calcd} 2.537 g cm^{-3}. Of 4450 reflections measured, 3415 reflections with $F_0 > 2\sigma F_0$ (PHILIPS PW 1100, $\lambda = 0.710\,69$ Å, $2\theta < 50°$, Lp and empirical ($\mu = 110$ cm^{-1}) absorption corrections) were used for the calculations. Refinement to $R = 0.074$, $R_{w(F)} = 0.072$ with H atoms ignored. The structure was solved by standard Patterson and difference Fourier methods.

Iron K-Edge EXAFS Data on $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_n$ ($n = 0$–2). The Structure of an Iron(IV) Complex of *o*-Phenylenebis(dimethylphosphine)

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Iron(IV) is a rare oxidation state, and relatively few thoroughly characterized compounds have been reported.[1] The presence of Fe(IV) in oxidized horseradish peroxidase was proposed over 30 years ago,[2] and the nature of the oxidation products of iron(III) porphyrins has remained a topic of considerable controversy. Recent studies have identified many of the one-electron oxidation products of iron(III) porphyrins as iron(III) porphyrin π-cation radicals; i.e., the oxidation is ligand rather than metal centered.[3-5]

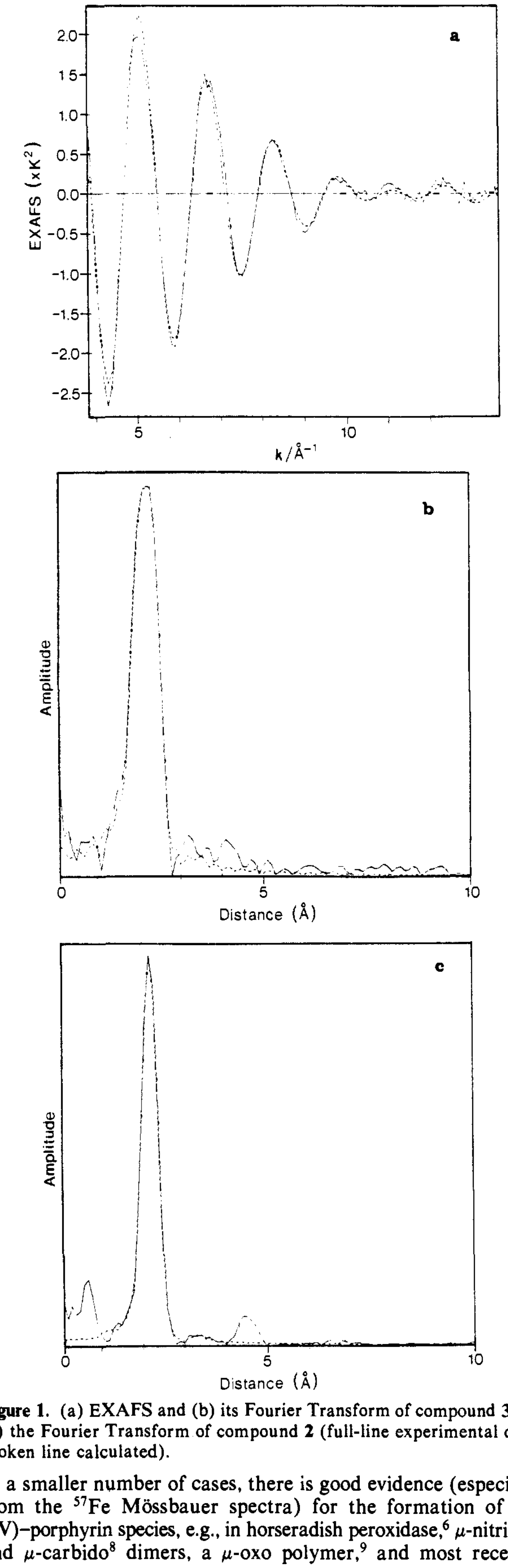

Figure 1. (a) EXAFS and (b) its Fourier Transform of compound **3** and (c) the Fourier Transform of compound **2** (full-line experimental data; broken line calculated).

In a smaller number of cases, there is good evidence (especially from the ^{57}Fe Mössbauer spectra) for the formation of Fe(IV)-porphyrin species, e.g., in horseradish peroxidase,[6] μ-nitrido-[7] and μ-carbido[8] dimers, a μ-oxo polymer,[9] and most recently

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Table I. Structural Data

complex	Fe–Cl, Å[a]	Fe–P, Å	σ^2, Å^2 [b]	technique	ref
$[PPh_4][FeCl_4]$	2.19		0.005	EXAFS	this work
$[AsPh_4][FeCl_4]$	2.182 (1)			X-ray	27
$[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]$ (**1**)	2.35	2.23	0.007, 0.006	EXAFS	this work
$[Fe(Me_2PCH_2CH_2PMe_2)_2Cl_2]$	2.352 (1)	2.241 (1), 2.230 (1)		X-ray	28
$[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]$ (**2**)	2.245	2.245	0.010, 0.010	EXAFS	this work
$[Fe(o\text{-}C_6F_4(PMe_2)_2)_2Cl_2][BF_4]$	2.234 (1)	2.292 (1), 2.295 (1)		X-ray	29
$[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_2$ (**3**)	2.16	2.33	0.007, 0.010	EXAFS	this work

[a] Using current data analysis programs, the errors in the EXAFS bond lengths are considered to be ±0.01–0.02 Å. [b] Debye–Waller parameter.

monomeric dialkoxy complexes.[10] The porphyrin ring system is special and it would be desirable to have structural data on simpler iron(IV) compounds. Examples of the latter type with anionic ligands are the oxo metalates Ba_2FeO_4, Na_4FeO_4,[11,12] dithiocarbamates $[Fe(R_2NCS_2)_3]^+$,[13-15] diselenocarbamates $[Fe(R_2NCSe_2)_3]^+$,[16] and 1,1-dithiolates $[Fe(S_2C_2(CO_2Et)_2)_3]^{2-}$.[17] Isolation of Fe(IV) complexes with neutral ligands is especially difficult and it is notable that, although electrochemical oxidation of $[Fe(L\text{–}L)_3]^{3+}$ (L–L = 2,2′-bipyridyl, 1,10-phenanthroline) to the 4+ cation is possible,[18] the electron removed is from a ligand orbital. The only neutral ligands complexed to Fe(IV) are *o*-phenylenebis(dimethylarsine) in $[Fe(o\text{-}C_6H_4(AsMe_2)_2)_2X_2][BF_4]_2$ (X = Cl, Br)[19] and its phosphorus analogue in $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][ReO_4]_2$,[20] for which ^{57}Fe Mössbauer spectra[21] and the magnetic data[19,20] support a $(t_{2g})^4$ formulation.

As part of our studies on high oxidation state complexes,[22] we have recently prepared Fe(IV) complexes of several diphosphines, details of which will be reported elsewhere. The $(t_{2g})^4$ configuration is rare among the 3d elements and the accompanying structural data are keenly sought,[23] but the instability of the Fe(IV) complexes (decomposition occurs in hours in the solid state at room temperature and in minutes in most solvents) has precluded the growth of single crystals for X-ray studies. However, we have recently shown that structural data on similarly unstable Ni(IV) diphosphine complexes can be obtained by using a combination of spectroscopic data and metal K-edge EXAFS.[24] Here we report a similar study of the series $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_n$ (n = 0–2) (compounds(**1**–**3**) which not only provides data for the Fe(IV) complex (n = 2) but also places the bond length changes in context as the metal's formal oxidation state changes from II to III to IV. Spectroscopic data[19,20,25] show that all three complexes are trans six-coordinate (*trans*-P_4Cl_2 complexes) and, in the treatment of the EXAFS data, the coordination number and donor atom arrangement was fixed. This removes some uncertainty in data interpretation due to the strong correlation between the Debye–Waller terms and the coordination number; such a correlation would cause particular difficulties for these systems in view of the similar back-scattering functions of phosphorus and chlorine.

EXAFS data at the iron K-edge were recorded at the Daresbury Synchrotron Radiation Source operating at an energy of 2.0 GeV with an average current of 160 mA. Phase shifts were calculated by using the ab initio approach described elsewhere,[26] and their reliability was established by interpretation of the EXAFS recorded for $[FeCl_4]^-$ and compounds **1** and **2**. For $[FeCl_4]^-$, the Fe–Cl bond length (Table I) determined by EXAFS agrees well with crystallographic data.[27] For compound **1** $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]$, both the Fe–Cl and Fe–P distances are in good agreement with the crystallographic data[28] for the related complex $[Fe(Me_2PCH_2CH_2PMe_2)_2Cl_2]$. However, there is some discrepancy between the Fe–Cl and Fe–P distances observed for compound **2** $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]$ and the results of the X-ray determination[29] (Table I) for the related complex $[Fe(o\text{-}C_6F_4(PMe_2)_2)_2Cl_2][BF_4]$. The EXAFS analysis of compound **2** could not distinguish between the Fe–P and the Fe–Cl distances and an average value of 2.245 Å was obtained, some 0.03 Å shorter than in the (tetrafluorophenyl)diphosphine complex. The inability of EXAFS to distinguish between the Cl and P shells is demonstrated by the sharpness of the peak in the Fourier transform (Figure 1c) and is undoubtedly due to the similar back-scattering of Cl and P, combined with the small differences in the shell distances.

The problem of distinguishing between Cl and P shells was *not* apparent for compound **3**, $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_2$. The Fourier transform of the EXAFS data (Figure 1b) especially when compared to that of compound **2** (Figure 1c) shows clear evidence for the two shells. The Fe–Cl and Fe–P bond distances which produced the optimum interpretation of the EXAFS data for compound **3** are shown in Table I.

Comparison of the Fe–Cl and Fe–P bond lengths in **1**, **2**, and **3** shows that, as the oxidation state of the iron increases, the Fe–Cl bonds shorten and the Fe–P bonds lengthen. The same trends

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(25) $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]$ (**1**) green powder, prepared from freshly reduced ethanolic $FeCl_2$ and the ligand under dinitrogen. Anal. Calcd for $C_{20}H_{32}Cl_2FeP_4$: C = 45.8, H = 3.8. Found: C = 45.7, H = 3.8. $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]$ (**2**) red crystals, prepared from $FeCl_3$ and the ligand in ethanol, followed by treatment with excess HBF_4 (30%). Anal. Calcd $C_{20}H_{32}BCl_2F_4FeP_4$: C = 39.4, H = 5.5. Found: C = 39.5, H = 5.5. $[Fe(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2][BF_4]_2$ (**3**) deep violet crystals, prepared by dissolving **2** moistened with a few drops of concentrated hydrochloric acid, in concentrated nitric acid at 0 °C, filtering, and precipitating the product with 40% HBF_4 at 0 °C. The solid was dried in vacuo in the dark. Anal. Calcd $C_{20}H_{32}B_2Cl_2F_8FeP_4$: C, 34.5; H, 4.5; Cl, 10.2. Found: C, 35.0; H, 4.7; Cl, 10.0. Magnetic moments: (**1**) diamagnetic, (**2**) 2.21 μB, (**3**) 3.01 μB (±0.05). IR spectra ν(Fe–Cl) (**1**) 349, (**2**) 377, (**3**) 384 cm^{-1}. Dynamic voltammetry reveals two reversible le oxidations of **1** at +45, +1430 mV vs. SCE in MeCN solution.

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have been observed in $[Mn(o\text{-}C_6H_4(PMe_2)_2)_2Cl_2]^{n+}$ (n = 1, 2).[20] The lengthening of the Fe–P bonds as the metal oxidation state increases is probably due to the decreasing Fe–P orbital overlap as the metal orbitals contract. Correspondingly, the shortening of the Fe–Cl bonds **1** < **2** < **3** reflects a stronger interaction with the σ and π donor orbitals of the chloride as the charge on the metal increases. Furthermore, it has been pointed out[28] that, for Fe(II) with the $(t_{2g})^6$, configuration there may be a destabilizing π-repulsion between the chlorine $p\pi$ and the filled metal acceptor orbitals which will decrease as the t_{2g} orbitals are progressively emptied. The strong axial compression observed in **3** by EXAFS also correlates well with the results of ^{57}Fe Mössbauer studies on the diarsine analogue, which concluded[21] that the complex possessed a $^3A_2$ ground state with a strengthening of the ligand field along the Cl–Fe–Cl axis compared with the Fe(II) and Fe(III) systems.

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C-Xe Bond Strength in the Methylxenonium Cation Determined from Ion Cyclotron Resonance Methyl Cation Exchange Equilibria

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Since the original discovery by Bartlett[1] of a species containing a XeF bond, a variety of other xenon-containing compounds have been prepared and characterized. Both ionic and covalent bond compounds have been synthesized involving bonds between xenon and boron,[2] fluorine,[3] nitrogen,[4] and oxygen.[5] In addition evidence has been presented for a C–Xe bond in $(CF_3)_2Xe$[6] and transient XeCl has been used in excimer lasers.[7] Despite the variety and number of xenon-containing compounds, however, very little quantitative information is available for bond dissociation energies of bonds to xenon. Very early kinetic experiments by Johnston[8] established Xe–F bond strengths in XeF_4, XeF_2, and XeF of 48, 54, and 11 kcal mol^{-1}, respectively. Later photoionization mass spectrometric appearance energy measurements were used to accurately determine $\Delta H_f°(XeF_2)$,[9] and a value for the Xe–F bond energy in XeF_2 of 55 kcal mol^{-1} was obtained.

Holtz and Beauchamp[10] have carried out ion-molecule reactions in H_2, Xe, and CH_3F mixtures in an ICR spectrometer and have observed eq 1, which establishes the methyl cation binding energy

$$CH_3FH^+ + Xe \rightarrow XeCH_3^+ + HF \qquad (1)$$

of Xe as greater than that of HF. On the basis of failure to observe the analogous reaction for CH_3ClH^+ (and the accepted thermochemical data at the time) a methyl cation binding energy for Xe of 43 ± 8 kcal mol^{-1} was deduced.

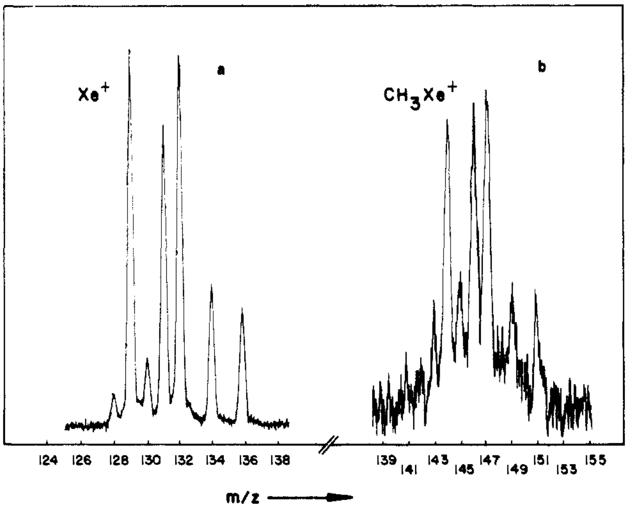

Figure 1. (a) Partial mass spectrum of Xe at a total pressure of 10^{-6} torr and 70-eV electron energy. (b) Time-delayed mass spectrum of the m/z 140–156 region for an 18:1 mixture of Xe/CH_3F at a total pressure of 2 × 10^{-6} torr, 200 ms following a 5-ms, 70-eV electron beam pulse.

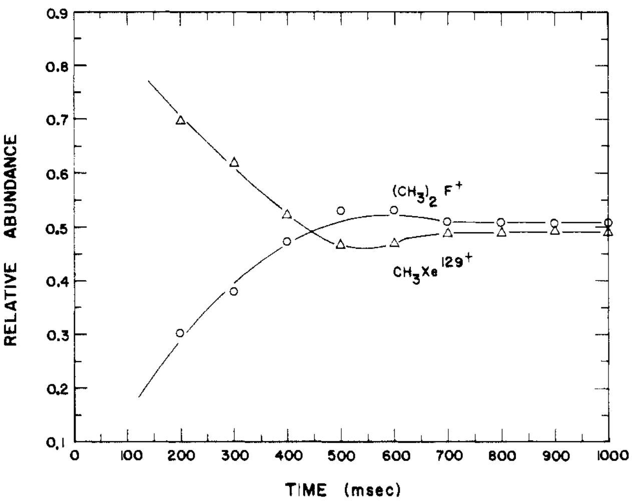

Figure 2. Variation of relative ionic abundances with time for an 18:1 mixture of Xe/CH_3F at a total pressure of 2 × 10^{-6} torr following a 5-ms, 70-eV electron beam pulse.

Recently a pulsed electron beam high-pressure mass spectrometric method[11] has been developed for the accurate determination of methyl cation binding energies through observation of methyl cation transfer equilibria. The binding energy of CH_3^+ to N_2 may be accurately determined from photoionization appearance energy measurements for the production of $CH_3N_2^+$ from azomethane, eq 2.[12] The observed threshold for $CH_3N_2^+$ production of 9.20

$$CH_3N{=}NCH_3 \xrightarrow{h\nu} CH_3N_2^+ + CH_3 \qquad (2)$$

± 0.03 eV and standard neutral thermochemistry[13] allow calculation of the methyl cation affinity of N_2 as 51.9 ± 1.7 kcal mol^{-1}. In the high-pressure mass spectrometer an ion-molecule reaction sequence, eq 3–5, in N_2–CH_3F mixtures in which N_2 is present

$$N_2^+ + CH_3F \rightarrow CH_3F^+ + N_2 \qquad (3)$$

$$CH_3F^+ + CH_3F \rightarrow CH_3FH^+ + CH_2F \qquad (4)$$

$$CH_3FH^+ + N_2 \rightarrow CH_3N_2^+ + HF \qquad (5)$$

$$CH_3N_2^+ + CH_3F \rightleftharpoons (CH_3)_2F^+ + N_2 \qquad (6)$$

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