the pore structure is known to yield a single NMR resonance, even when more than one type of ion is present. It should be noted that the shift is probably due to local interactions involving the cations as the cubic symmetry of the unit cell is preserved and the local geometry of the silicon atoms is unchanged. Figure 1C,D shows the corresponding ^{29}Si MAS NMR spectrum and XRD pattern of the same system after allowing it to equilibrate for 18 h. Both spectra show single peaks indicative of there being a single species of average cation content present rather than a mixture. A previous report[4] of such a change has been made from XRD measurements and this is now confirmed for both the short- and long-range aspects of the structure. The species of average composition which results must have been formed from simultaneous migration of the different cations in opposite directions between the two sets of crystallites, purely from the macroscopic mechanical contact between the crystallites. The changes are reproducible, with the position of the NMR and XRD absorptions of the resulting "average" species depending, in a predictable manner, on the relative concentrations of the starting materials as would be expected. Scanning electron microscopy (SEM) confirms that the crystals remain intact unless severe conditions are used. In the present work a plastic ball was used to ensure that little or no degradation occurred when this apparatus was used.

Several variables are important in determining the rate of reaction: First, the rate depends on the amount of mechanical mixing of the sample. For example, mixing Li$^+$A and Na$^+$A, with particle size 1–2 μm, for 10 s in a wigglebug will give complete exchange although SEM indicates a small loss of crystallinity ($<1\%$) due to the mechanical shock of mixing, while simply mixing the two sets of crystals by lightly stirring them together gives a system which takes 24 h to come to equilibrium with no loss in crystallinity. Second, the degree of hydration is important. For example, it can take several weeks for a mixture of dehydrated Li$^+$A and Na$^+$A (20–25-μm particle size) to reach equilibrium. However, when the same sets of crystals are fully hydrated, complete exchange will be attained after mixing for only 30 s in a wigglebug. Third, the reaction is very dependent on the crystallite size; small crystals (1–2 μm) reach equilibrium immediately while large (20–25 μm) crystals take 24 h to reach equilibrium under the same conditions (crystals partially dehydrated and mixed in wigglebug for 5 s). In general, although difficult to quantify, the reaction is surprisingly fast; for example, complete exchange occurs in approximately 5 min for a mixture of Li$^+$A and Na$^+$A (5-μm particle size) that has been mixed for 5 s in a wigglebug.

The profiles of the NMR and XRD spectra at intermediate times are complex and reflect the mechanism of the migration process. Since both long- and short-range orderings are being monitored by these experiments, it is hoped that a detailed picture of the mechanism will result from this data and such studies are currently in progress.

Preliminary results indicate that similar cation migrations occur between other pairs, for example, Li$^+$A and Na$^+$Y as well as between Li$^+$A and Na$^+$mordenite.

Further investigations of these systems are being carried out, but there are important implications in the semiquantitative results presented here concerning the practical use of zeolites in industrial processes: Often they are used together with "binders", usually natural clays, to increase the particle size and ease of handling. Those natural clays contain a number of cations, including transition-metal ions, and the present results suggest that migration of these species into the zeolite lattice is possible, especially if they are extruded under pressure with the binder. Thus the zeolite under reaction conditions may not have the same physical or physicochemical properties as the pure species used without additives.

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Pulse Radiolysis Studies of Alkaline Fe(III) and Fe(VI) Solutions. Observation of Transient Iron Complexes with Intermediate Oxidation States

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With the exception of some isolated studies on aqueous Fe(IV) in the 1960's,[1,2] the Fe(IV)/Fe(V) species have received little attention until quite recently.[3] Interest in these oxidation states has been stimulated by the finding that certain Fe(V) (or Fe(IV) cation radical) porphyrins[3,4] are the active intermediates in biological hydroxylation reactions. In nonbiological systems less exotic iron complexes such as Fe(EDTA)$^-$ perform silimar functions in the presence of H_2O_2. The intermediacy of Fe(IV), or the ferryl ion, FeO^{2+}, rather than the hydroxyl radical has been postulated to explain the specificity of these systems.[3,5] Recent thermodynamic calculations suggest that FeO^{2+} should be accessible in aqueous solution in the presence of suitable ligands.[6] In this paper we wish to report the first spectroscopic evidence for complexes containing iron formally in the IV and V oxidation states in the presence of a simple ligand, i.e., OH^- and $P_2O_7^{4-}$ in alkaline solution.

These transient species are obtained by pulse radiolysis of alkaline ferric (Fe(III)) and ferrate (Fe(VI)) solutions by using the hydroxyl radical or its conjugate base, O^-, and the aquated electron, e_{aq}^-, as the respective oxidizing and reducing agents. Dilute solutions containing monomeric Fe(III), as $Fe(OH)_3$/$Fe(OH)_4^-$,[7] and/or FeO_4^{2-} were prepared electrolytically in NaOH solutions (NaOH, 99.999%; G. F. Smith). A current of 500–1000 mA at 8–10 V was applied for 1–3 h to an iron anode (wire) in a 200-mL compartment that was separated from the cathode compartment (Pt wire) by a glass frit. Continuous evolution of dioxygen at the anode ensured the absence of Fe(II) in these solutions. Total iron concentrations were determined spectrophotometrically as the tris(*o*-phenanthroline)iron(II) complex following reduction with dithionite; ferrate (VI) concentrations were monitored by its absorption spectrum (vide infra). In chilled (~5 °C) 5 M NaOH, solutions of 50 μM Fe(VI) (60 μM total Fe) were obtained. In 1 M NaOH solutions 35 μM of Fe(III) were found after decomposition of any Fe(VI); the latter was not determined in these conditions because of its instability. These solutions were clear, stable, and free of colloidal iron. The only significant contaminant was a trace of carbonate which proved not to inhibit the reactions of interest. These solutions were pulse-irradiated with 2-MeV electrons from a Van de Graaf accelerator. The radiolysis of water is denoted by eq 1 where *G*

$$H_2O \rightsquigarrow e_{aq}^-\ (2.65),\ OH\ (2.75),\ H\ (0.65),\ H_2\ (0.45),\ H_2O_2\ (0.72) \quad (1)$$

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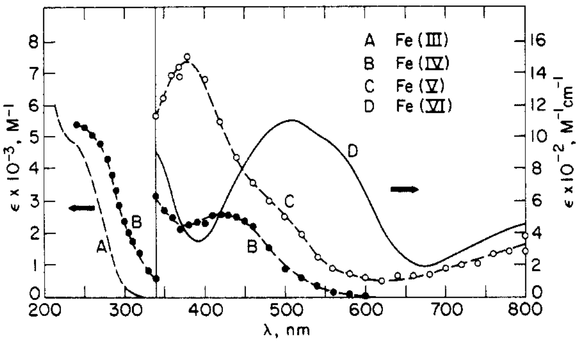

Figure 1. Absorption spectra of iron(III), -(IV), -(V), and -(VI) in 1–5 M NaOH. (A) iron(III) hydroxide spectrum in 1 M NaOH at 25 °C; (B) iron(IV) hydroxide/iron(IV) pyrophosphate spectrum obtained in reactions 2 and 5, respectively; (C) Fe(V) spectrum in 5 M NaOH, 15 °C, obtained by reduction of Fe(VI) by the hydrated electron; (D) spectrum of Fe(VI) in 5 M NaOH.

values (or molecules formed per 100 eV of energy dissipated in the medium) are given in parentheses.[8] In strong alkali, H atoms are converted to e_{aq}^- ($H \rightleftharpoons e_{aq}^- + H^+$; $pK_a = 7.85$)[9] and OH radicals deprotonate: $pK_a(OH/O^-) = 11.9$.[10] Spectrum A in Figure 1 is that of $Fe(OH)_4^-$. Pulse radiolysis of an N_2O-saturated Fe(III) solution (pH 10.7–14) resulted in the transient spectrum B in Figure 1. We attribute spectrum B to the product of reaction 2

$$O^-/OH + Fe(OH)_4^- \xrightarrow{k_2} FeO(OH)_n^{2-n} + (4-n)OH^-/(3-n)OH^- + H_2O \quad (2)$$

which is formulated as the *n*-hydroxyl ferryl complex, where by convention iron is in the +4 oxidation state.

It is assumed in eq 2 that Fe(IV) is present in monomeric form analogous to monomeric vanadium(IV) which is of the form $VO(OH)_3^-$ in 1 M NaOH.[11] The decay of $FeO(OH)_n^{2-n}$ is first order ($k_{decay} = 2 \pm 1$ s^{-1}; 1 M NaOH, 25 °C) and is independent of $[Fe(OH)_4^-]$ in the range 10–35 μM. Iron(IV) becomes slightly more stable as $[OH^-]$ is increased. Colloidal Fe(III) appears to be unreactive in reaction 2. Attempts to measure the formation and stability of Fe(IV) at lower $[OH^-]$ were made with a rapid mixing device that mixes Fe^{3+} (50–100 μM Fe(III)) in dilute $HClO_4$) and dilute NaOH. The solutions were pulsed at pH ≥10.7 before precipitation of $Fe(OH)_3$ could seriously interfere; although the observed spectra were similar to those found in 1 M NaOH, the kinetics were not resolved. At still lower pH, however, the precipitation of $Fe(OH)_3$ proved too rapid for our present premixing arrangement. Overall, the presence of CO_3^{2-} interferes with the direct measurement of k_2 as the CO_3^- radical which is formed in competition with reaction 2[12] also reacts with Fe(III) to form Fe(IV). The latter reaction goes to completion within ~1 ms when an excess (up to 0.02 M) K_2CO_3 is present at pH >13.

When 5–10 μM oxygen was added to the N_2O-saturated solutions and $[CO_3^{2-}]$ kept small, the rather unreactive ozonide radical was formed from the O^- radical via eq 3, where $k_3 = 3$

$$O^- + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} O_3^- \quad (3)$$

$\times 10^9$ M^{-1} s^{-1}[10] and $k_{-3} = 3.3 \times 10^3$ s^{-1}.[13] In the presence of 20 μM $Fe(OH)_4^-$ in 0.2 M NaOH, O_3^- disappears with an observed rate of 1.8×10^3 s^{-1} with simultaneous formation of Fe(IV). We concluded that OH/O^- are the reactive species in this system and that a lower limit of $k_2 \geq 8.5 \times 10^7$ M^{-1} s^{-1} = 1.8×10^3 s^{-1}/[Fe(III)] can be calculated for these conditions.

Although it is not possible to assign an oxidation state from the electronic spectrum, certain considerations support our description of the product of reaction 2 as an Fe(IV) complex. Though strongly oxidizing ($E°(O^-,H_2O/2OH^-) = 1.7$ V)[14a,b] O^- radicals cannot oxidize by direct electron transfer[15] but most likely react by hydrogen abstraction from H_2O/OH^- and/or substitution of H_2O/OH^- bound to Fe(III) resulting in a relatively stable product. If, as is suggested by our results and an earlier ^{60}Co radiolysis study of the ferrate(VI) system,[16] the Fe(IV) in alkaline media is reduced to Fe(III) by the oxidation of water (or OH^-), then reaction 2 might be recast as an equilibrium with forward and reverse rates at least approximately equal to k_2(obsd) and k(Fe(IV)decay), respectively. This leads to an estimated stability constant for formation of the iron–oxygen bond from Fe(III) and O^- of about 10^8 M^{-1}. This stability can be best explained if there is substantial covalent bonding, e.g., p_π–d_π overlap between a half-filled metal t_{2g} orbital and the unpaired 2p electron of O^-.[17] This suggests that the ligand–radical resonance form, Fe^{III}–O^-, makes a smaller contribution than $Fe^{IV}{=}O$ to the formal oxidation state. However, the resonance form Fe^{III}—O^-, being kinetically less stable to dissociation, might be of importance in the reactivity of ferryl complexes.

Preliminary oxidation studies of Fe(III) by the pyrophosphate radical at pH 10.4

$$H_2O/OH + P_2O_7^{4-} \xrightarrow{[H^+]} P_2O_7^{3-} + H_2O/OH^- \quad (4)$$

$$P_2O_7^{3-} + Fe(III) \rightarrow Fe(IV) + P_2O_7^{4-} \quad (5)$$

yielded a spectrum similar to that obtained in reaction 2. The spectral similarity of the products of reaction 2 and 5, which have different ligands, argues in favor of a change in the oxidation state of iron, i.e., Fe(III) to Fe(IV).

Pulse radiolysis of 50 μM ferrate solutions in 5 M NaOH degassed with argon resulted in the absorption spectrum C of Figure 1. The corresponding absorbance of the nonirradiated FeO_4^{2-} solution is shown in spectrum D.[18] Although no suitable scavenger of O^- compatible with FeO_4^{2-} was found, at low [Fe(VI)] only e_{aq}^- is reactive (O^- reduces Fe(VI) to Fe(V) at ~3% of the rate of e_{aq}^-).[16] The one-electron reduced species, formally Fe(V), which we provisionally formulate as FeO_4^{3-}, is formed by reaction 6 which occurs at the diffusion-controlled rate of k_6 =

$$FeO_4^{2-} + e_{aq}^- \xrightarrow{k_6} FeO_4^{3-} \quad (6)$$

$(2.0 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}. Superoxide radical, O_2^-, is also an effective reductant for producing iron(V) under these conditions. Fe(V) decays completely to Fe(III) by first-order kinetics with $k_{decay} = 4 \pm 1$ s^{-1} at 15 °C in 5 M NaOH. The longer lived iron(IV) was not observed as an intermediate of the decomposition of iron(V).

The spectrum of iron(IV) has one strong absorption peak at $\lambda_{max} = 240$ nm ($\epsilon \sim 5500$ M^{-1} cm^{-1}) which is most likely a charge-transfer band and a weaker transition at $\lambda_{max} = 420$ nm; $\epsilon = 520 \pm 20$ M^{-1} cm^{-1}. Iron(V) has a significant absorbance in the UV (not yet resolved), $\lambda_{max} = 390$ nm ($\epsilon = 1500 \pm 100$ M^{-1} cm^{-1}), and a band at $\lambda > 600$ nm. This spectrum seems compatible with a preferred tetrahedral geometry as other high-valent metal oxoanions also absorb at long wavelengths (e.g., CrO_4^{3-}, MnO_4^-, and FeO_4^{2-}).

Our preliminary results indicate that both Fe(IV) and Fe(V) have significant lifetimes when complexed with a simple ligand and are thus plausible intermediates in iron-catalyzed oxidations of organic compounds. The stabilizing effect of hydroxide ions on a highly oxidizing metal ion is not unusual. Further investigation of this system may lead to a more detailed knowledge of the thermodynamics and structure of these important oxidation states of iron.

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Pulse radiolysis allows us to study the reactions of Fe(IV) and Fe(V) in the absence of excess strong oxidants (e.g., H_2O_2). The immediate objective of these studies is not only to find other ligands and methods that will allow generation/stabilization of the Fe(IV) and Fe(V) species but also to measure their reactivity with various organic compounds. The characterization of the Fe(IV)/Fe(V) oxidation states in simple complexes will hopefully lead to the understanding of these iron forms in more complex systems.

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Registry No. $Fe(OH)_4^-$, 29145-79-7; FeO_4^{2-}, 16836-06-9; $P_2O_7^{3-}$, 99783-30-9; FeO_4^{3-}, 37114-36-6; Fe^{3+}, 20074-52-6; Fe^{6+}, 14127-55-0.

Additive Trans Influences of the Axial Ligand and Metal-Metal Bond in a Diplatinum(III) Complex Leading to an Asymmetric Structure with Penta- and Hexacoordination of the Two Metals

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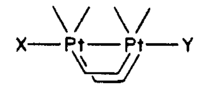
Dinuclear Pt(III) complexes represent a relatively new class of compounds. In all crystallographically characterized examples reported so far, the two metals possess hexacoordination, regardless of whether the bridging ligands are symmetric (e.g., CF_3COO^-,[2] SO_4^{2-},[3] $H_2P_2O_5^{2-}$,[4] HPO_4^{2-},[5]) or asymmetric (e.g., pyridin-2-one,[6] 1-methyluracil,[7] pyrimidine-2-thione[8]) or if, in the latter case, they form a head–head,[6a] a head–tail arrangement,[6b,7] or a combination of both.[8] We herewith report the first crystal structure of a diplatinum(III) complex, $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_3{\cdot}H_2O$ (with 1-MeU = monoanion of 1-methyluracil, $C_5H_5N_2O_2$), having one Pt atom hexacoordinated and the other Pt atom pentacoordinated only. Similar asymmetric structures have been proposed, on the basis of NMR spectroscopic evidence,[9] for $CF_3CO_2^-$-bridged diplatinum(III) complexes.

We believe that the difference in Pt coordination numbers in the here described complex is a consequence of the additive effects of the structural trans influence of the nitro ligand in the axial position of one Pt *and* the Pt–Pt bond for the following reasons: (i) Both the nitro ligand and the Pt–Pt unit on their own excert a strong trans influence.[6,10] (ii) In a related complex with head–tail orientation of the bridging ligands, $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3{\cdot}5H_2O$,[7] the Pt–$OH_2$ bond trans to the O_2N–Pt–Pt unit is extremely long already, 2.253 (9) Å. This distance compares with 2.176 (11) and 2.171 (11) Å in the corresponding complexes with the NO_2^- ligand replaced by ONO_2^-[11] and 2.122 (6) Å in a related complex of α-pyridone.[6a] (iii) If the nitro ligand of the title compound is substituted by a ligand of lower trans influence, e.g., Cl^-,[12] both Pt atoms become hexacoordinated, thus ruling against steric arguments (vicinity of exocyclic O2′ oxygens of 1-MeU rings) for a lower coordination number of the second Pt.

Table I. Pt–Pt Separations in 1-Methyluracilato-Bridged Diplatinum(III) Complexes



	X	Pt–Pt, Å	Y	ref
head–head	NO_2^-	2.607 (1)		*a*
	Cl^-	2.573 (1)	Cl^-	*b*
	Cl^-	2.543 (1)	Cl^-	*c*
head–tail	NO_2^-	2.574 (1)	OH_2	*d*
	ONO_2^-	2.556 (1)	OH_2	*e*
	ONO_2^-	2.560 (1)	OH_2	*e*

[a] This work. [b] $[Cl(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl]Cl_2$.[12] [c] $Cl(NH_3)_2Pt(1\text{-}MeU)_2PtCl_3$.[12] [d] $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3$.[7] [e] Two modifications of $[(ONO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2(OH_2)](NO_3)_3$.[11]

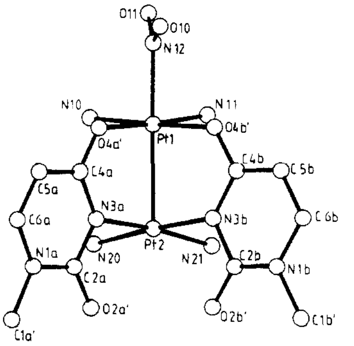


Figure 1. PLUTO drawing of the cation $[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2]^{3+}$ of the title compound.

In Table I the Pt–Pt distances of six diplatinum(III) complexes, containing two 1-MeU bridges each, are listed. The data confirm previous findings[6] on the structural trans influence of the nitro ligand on the Pt–Pt separation, but they suggest also that only head–head or head–tail dimers should be compared and that substitution of the equatorial NH_3 ligands (e.g., by Cl^-, footnote c in Table I) affects the Pt–Pt bond length as well.

Formation of the title compound is achieved by oxidation of the diplatinum(II) complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_2$[13] with HNO_3.[14] Orange crystals of the title compound are diamagnetic and EPR-inactive. The compound was characterized by elemental analysis,[15] X-ray analysis,[16] and

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