the total integrated area of the two EPR signals remains constant.

(20) For an example of valence isomerism between bent and linear coordinated NO in cobalt complexes see Collman, J. P.; Farnham, P.; Dolcetti, G. *J. Am. Chem. Soc.* **1971**, *93*, 1788.

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Heats of Formation of SO_2Cl^- and $(SO_2)_2Cl^-$

Sir:

Currently, ion-molecule reactions are the objects of intense investigations. Results from these studies have proven to be valuable in expanding the availability of gas-phase thermochemical values such as electron affinities and heats of formation. In particular, data from the study of ion-neutral association reactions provide a foundation for understanding subjects such as ion solvation, atmospheric ion chemistry, nucleation phenomena, and ion-molecule interactions.[1,2]

Recently, Robbiani and Franklin[3] have reported upper limits to the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ based on observations of the ion-molecule reactions

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \qquad (1)$$

$$SO_2Cl^- + SO_2Cl_2 \rightarrow S_2O_4Cl^- + Cl_2 \qquad (2)$$

From these reactions, they compute $\Delta H_f^\circ(SO_2Cl^-) \leq -136$ kcal/mol and $\Delta H_f(S_2O_4Cl^-) \leq -220$ kcal/mol by postulating that the observed $S_2O_4Cl^-$ is formed by reaction 2. (The authors inadvertently use the upper limit for $\Delta H_f^\circ(SO_2Cl^-)$ as a lower limit to conclude that this value must be *near* −135 kcal/mol.)

In our laboratory, a high pressure mass spectrometric technique has been employed[4] for determining the thermodynamic quantities of gas-phase reactions of the form

$$A^- \cdot B_n + B \rightleftharpoons A^- \cdot B_{n+1} \qquad (3)$$

Briefly, ions are formed in a high pressure region, typically 5 to 15 Torr, and focused into a thermally controlled reaction cell. The pressure is sufficiently high such that the ions reside in this cell for a time adequately long for clustering reactions to equilibrate. The ions leak through a small orifice (typically 75-μ diameter) into a high vacuum region where they are mass analyzed and counted. From the ion intensities and known partial pressure of the clustering neutral, the equilibrium constant $K_{n,n+1}$ is determined.

Among the reactions which have been recently studied are the first four addition reactions (n = 0-3) of SO_2 onto Cl^- This work will be presented in greater detail in a future publication. From the enthalpy change $\Delta H^\circ_{n,n+1}$ for the first two of these reactions (−21.8 for $n = 0$ and −12.3 kcal/mol for $n = 1$) and from the heat of formation of Cl^- and SO_2, the heats of formation of SO_2Cl^- and $(SO_2)_2Cl^-$ can be computed. These values are listed in Table I.

The heats of formation in the present study are well below the upper limit previously published by Robbiani and Franklin[3] and are, therefore, consistent with their results. The value of $-\Delta H^\circ_{0,1}$ for reaction 3 is 21.8 kcal/mol and is equivalent to $D(SO_2-Cl^-)$. Robbiani and Franklin[3] concluded that this value was small (~5 kcal/mol) from their erroneous $\Delta H_f^\circ(SO_2-Cl^-)$. Nonetheless, $D(SO_2-Cl^-)$ is still somewhat less than $D(Cl-Cl^-)$ which is 27 kcal/mol. Therefore, their expectation that some of their observed $SO_2Cl_3^-$ is formed by the reaction of SO_2Cl^- with SO_2Cl_2 may still be valid.

Table I. Heats of Formation

M	$\Delta H_f^\circ(M)$, kcal/mol	ref
SO_2	−70.94	5
Cl^-	−58.8	5
SO_2Cl^-	−151.5	this work
$(SO_2)_2Cl^-$	−234.8	this work

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Formation of Porphyrin Ferryl (FeO^{2+}) Complexes through the Addition of Nitrogen Bases to Peroxo-Bridged Iron(III) Porphyrins

Sir:

The ferryl group $(Fe^{IV}=O)^{2+}$, or a protonated form thereof, has been frequently postulated as an intermediate in the mechanism of action of peroxidases, particularly in the identity of compound II of horseradish peroxidase, and in the autoxidation of Fe(II).[2] Complexes of Fe(IV) are rare[3] and no well-characterized, low molecular weight complexes containing the ferryl group are available for detailed study.[4] We recently reported on spectroscopic characterization of the Fe(III) peroxo-bridged complex, $PFeO_2FeP$ (P = a porphyrin dianion), which is formed by the addition of dioxygen to unligated PFe in toluene solution at low temperature.[5] We now report that nitrogeneous bases react with $PFeO_2FeP$ to yield new complexes which appear best described as ferryl complexes.

Addition of *N*-methylimidazole (Me-Im) to $TmTPFeO_2FeTmTP$ (TmTP = dianion of *meso*-tetra-*m*-tolylporphyrin) at −80 °C in toluene solution produces a new complex **1** $(Me\text{-}ImTmTPFeO)_x$, whose unique ^1H NMR and electronic spectra are shown in Figures 1 and 2, respectively. Titration of *N*-methylimidazole into a solution of $TmTPFeO_2FeTmTP$ reveals that 2 mol of base are required to consume all of the peroxide-bridged dimer originally present. Addition of further *N*-methylimidazole results in the growth of peaks characteristic of the free base, thus demonstrating that exchange between free *N*-methylimidazole and the newly formed iron complex is slow. The peaks due to coordinated Me-Im have not been resolved. **1** is indefinitely stable (>1 week) at −80 °C, while above −30 °C it decomposes to TmTPFeOFeTmTP at an appreciable rate.[6] The solution magnetic susceptibility of **1** measured at 360 MHz using the Evans technique[7] is 2.9 ± 0.1 μ_B/iron ion at −52 °C and is invariant down to −90 °C. Moreover the temperature dependence of the porphyrin paramagnetic shifts strictly follows the Curie law[7] over a larger temperature range (−85 to +15 °C) as is shown in the insert of Figure 1. Hence the iron ions exist in well-defined paramagnetic, noninteracting states.

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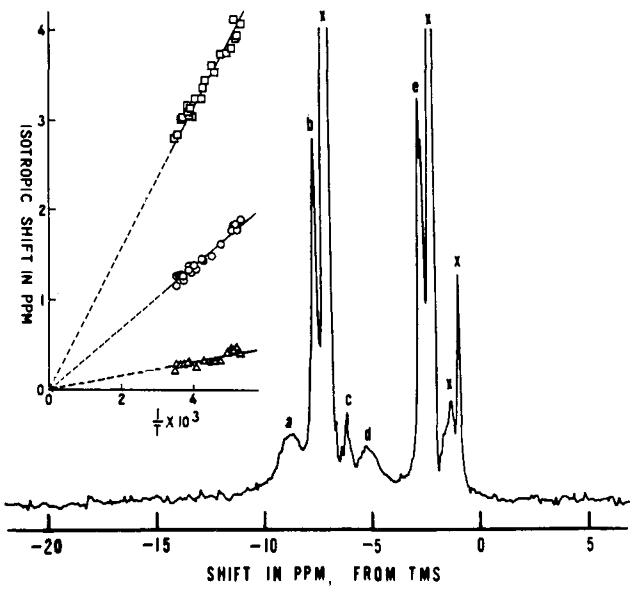

Figure 1. The 100-MHz ^1H NMR spectrum of **1** in toluene-d_8 at 200 K in the presence of excess Me-Im. The resonance assignments are (a) ortho phenyl hydrogens, (b) meta and para phenyl hydrogens, (c) uncoordinated Me-Im, (d) pyrrole hydrogens, (e) meta methyl hydrogens, (x) resonances from the solvent. Resonance e is absent in $(Me\text{-}ImTPPFeO)_x$ (TPP = dianion of *meso*-tetraphenylporphyrin). Resonances a, b, and e are absent in the spectrum of $[Me\text{-}ImTP(d_{20})PFeO]_x$. The split methyl resonance e is characteristic of metalloporphyrins having unsymmetrical coordination with respect to the porphyrin plane. The insert on the upper left shows the temperature dependence of the absolute paramagnetic shifts for **1**: □, peak d upfield shift; ○, peak a, downfield shift; △, peak b downfield shift.

Frozen solutions of **1** at 77 K do not display an electron spin resonance spectrum.

Related complexes, $(BTPPFeO)_x$, with B as pyridine or piperidine, form upon addition of these bases to $TPPFeO_2$-FeTPP at −80 °C. The electronic spectra, ^1H NMR spectra, and magnetic susceptibility of these two species are very similar to those reported above **1**. Under similar conditions at −80 °C in toluene solution there is no reaction between $TPPFeO_2FeTPP$ and either thiols or organic sulfides.

Probable structures for **1** are A and B. The dimer A would result from direct addition of the nitrogen bases to the intact peroxide-bridged complex, while the existance of B requires cleavage of an O–O bond. The susceptibility measurements on **1** are consistent only with a triplet ground state for the complex.[9] Consequently a low-spin Fe(IV) formulation is the most reasonable spin/oxidation state assignment for the metal.[10] To achieve the Fe(IV) state the peroxo O–O bond must be broken. The paramagnetic behavior of **1** also is consistent with a monomeric species and contrasts with the antiferromagnetic behavior of $TPPFeO_2FeTPP$[5] and TPPFeO-FeTPP[11] which have magnetic moments of 2.6 and 1.5 μ_B at −50 °C with values of the antiferromagnetic coupling constant $2J$ of 265 and 380 K, respectively. The magnetic susceptibility and electronic spectra also resemble closely those properties displayed by compound II of horseradish peroxidase.[12,13]

$$\underset{\textstyle A}{B(TmTP)FeO_2Fe(TmTP)B} \qquad \underset{\textstyle B}{BTmTPFeO}$$

Further support for the monomeric formulation for **1** comes from its reaction with TmTPFe. At −80 °C, **1** reacts instantaneously with TmTPFe to generate quantitatively TmTPFeOFeTmTP and free B according to eq 1. These data establish the iron to oxygen ratio in **1** as 1:1. In contrast to the rapid occurrence of reaction 1, solutions of $PFeO_2FeP$ and PFe show no indication of reaction after being mixed and held at −80 °C for 2 days. The large difference in kinetic reactivity of **1** and $PFeO_2FeP$ toward PFe suggests that the oxo ligand of **1** is more readily accessible for attack by Fe(II) and offers further support for the postulated ferryl structure.

$$BPFeO + PFe \rightarrow B + PFeOFeP \qquad (1)$$

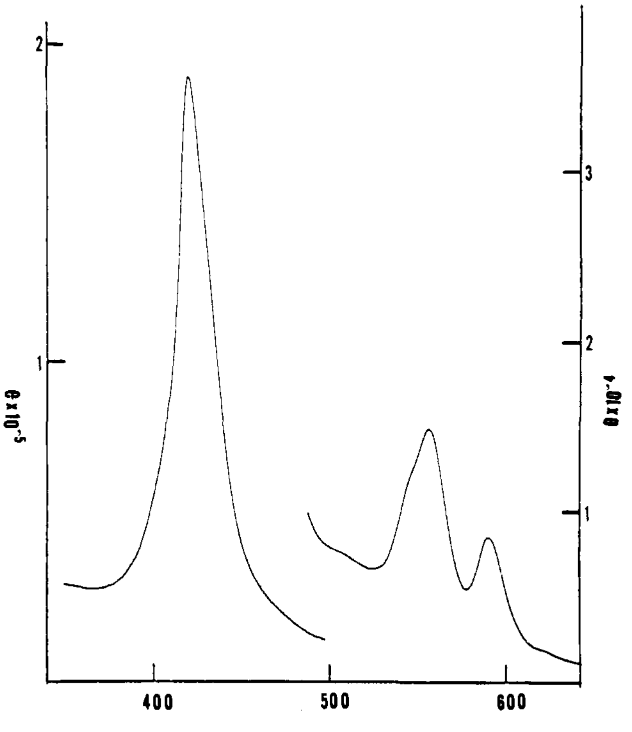

Figure 2. The visible spectrum of **1** in toluene solution at 183 K. The extinction coefficients are calculated per iron.

The formation of $PFeO_2FeP$ and **1** emphasizes the importance of the sequence in which substrates interact with PFe in determining the stoichiometry and structure of the products. When dioxygen is added to FeP after the addition of a nitrogenous base, the reversible dioxygen carrier $BPFeO_2$[14] is formed at low temperature and upon warming is directly converted into PFeOFeP. When the order of substrate addition is reversed, $PFeO_2FeP$ first forms and this in turn reacts with base to give **1** rather than diamagnetic $BPFeO_2$.

The chemical reactivity of **1** is under further investigation.

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Association of d^6 and d^8 Metal Complexes in Solution. Formation of (p-$CH_3C_6H_4NH_2$)$Ir(CO)_2Cl$/(p-$CH_3C_6H_4NH_2$)$Ir(CO)_2ClI_2$

Sir:

Reactions between metal complexes are now realized to be of significance to a variety of chemical processes including electron transfer,[1] metal-metal bond formation in both clusters[2] and chain compounds,[3] reductive elimination,[4] and ligand substitution. An example of the latter class is the substitution reactions of the six-coordinate d^6 complexes of the platinum metal [particularly Pt(IV)].[5,6] For these reactions, catalysis by planar d^8 complexes of the same metal occurs and a halo-bridged species involving the d^6 and d^8 reaction partners has been postulated as part of the reaction mechanism.[7] However, direct observation of the halo-bridged species has not been reported.[8] We now describe a pair of d^6 [Ir(III)] and d^8 [Ir(I)] complexes which associate in solution through a halo bridge.

Oxidation of (p-$CH_3C_6H_4NH_2$)$Ir(CO)_2Cl$, **1** ($\nu_{C\equiv O}$ 2086, 2004 cm^{-1} in CH_2Cl_2 solution, 2090, 2027 in Nujol mull), which has been extensively used as a precursor of Ir(I) compounds,[9] with an excess of iodine produces six-coordinate brown (p-$CH_3C_6H_4NH_2$)$Ir(CO)_2ClI_2$,[10] **2** ($\nu_{C\equiv O}$ 2151, 2105 in CH_2Cl_2 solution, 2143, 2090 cm^{-1} in Nujol mull). The electronic spectra of dichloromethane solutions of mixtures of **1** and **2** show features which are not present in the spectra of the individual components. In Figure 1 the new absorption characteristic of adduct formation is seen at 490 nm. This feature develops immediately upon mixing of **1** and **2**. Analysis of the concentration dependence of this band indicates that the adduct **3** is formed via

$$\underset{\textbf{1}}{(CH_3C_6H_4NH_2)Ir(CO)_2Cl} + \underset{\textbf{2}}{(CH_3C_6H_4NH_2)Ir(CO)_2ClI_2} \rightleftharpoons \underset{\textbf{3}}{(CH_3C_6H_4NH_2)_2Ir_2(CO)_4Cl_2I_2} \quad (1)$$

with an equilibrium constant of 5000 (±300) and ϵ for **3** at 490 nm of 6000 (±300). The stability of **3** is solvent dependent. It forms in dichloromethane, chloroform, and benzene but does not form in acetone or acetonitrile. The adduct **3** may be isolated as fine green crystals[11] with a metallic reflectance. These may be obtained by addition of cyclohexane to a concentrated dichloromethane solution of equimolar amounts of **1** and **2** or by oxidizing **1** in dichloromethane solution with one half of a molar amount of iodine followed by crystallization through the addition of cyclohexane. The adduct **3** is diamagnetic and shows no electron spin resonance spectrum as a solid or in solution. The formation of **3** cannot be ascribed to a tendancy for **1** to add ligands indiscriminately. Treatment of **1** with iodide results in substitution of iodide for chloride, but a five-coordinate complex is not detectable. Likewise **1** does not form an adduct with iodobenzene or chlorobenzene.

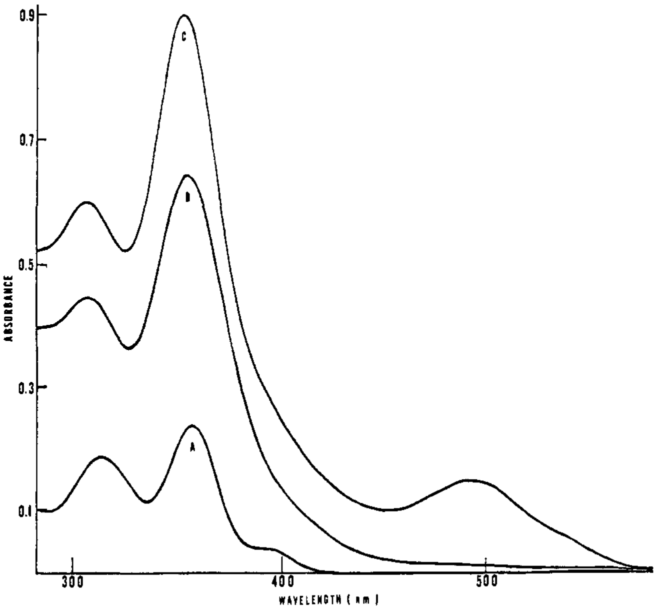
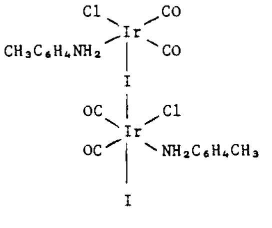
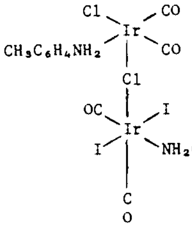


Figure 1. The electronic spectra of (a) 0.75 mM (p-$CH_3C_6H_4NH_2$)-$Ir(CO)_2Cl$; (b) 0.75 mM (p-$CH_3C_6H_4NH_2$)$Ir(CO)_2ClI_2$; (c) 0.75 mM (p-$CH_3C_6H_4NH_2$)$Ir(CO)_2Cl$ and 0.75 mM (p-$CH_3C_6H_4NH_2$)Ir-$(CO)_2ClI_2$. The solvent is dichloromethane throughout and the cell path length is 1.0 mm.

Structural information about **3** is available from its infrared spectra. In dichloromethane solutions prepared either by mixing **1** and **2** or by dissolving **3** there are no absorptions in the CO stretching region (2200-1600 cm^{-1}) other than those due to **1** and **2**. Additionally the carbonyl stretching absorptions of solid **3** as a Nujol mull (2133, 2087, 2080, 2009 cm^{-1}) occur at similar energies as were found for **1** and **2** individually. These observations eliminate the carbonyl groups as acting as bridges between the two iridium centers, Moreover, since the carbonyl stretching vibrations are sensitive to the iridium oxidation state, the data indicate that the individual iridium ions have undergone only minor perturbations in forming **3**. The data are inconsistent with the occurrence of a redox condensation to form a metal-metal-bonded Ir(II) dimer.[3] Consequently we propose a halo-bridged structure, either A or B for **3** with the iodo-bridged structure A favored. **3** must derive stability from some degree of charge transfer between the two metal complexes.



A



B

The behavior of these iridium complexes contrasts to the one other system so far described in which a d^8 and d^6 pair of complexes associate in solution. In that case reaction of $Rh(CNR)_4^+$ with $Rh(CNR)_4I_2^+$ yields either $Rh_2(CNR)_8I_2^{+2}$ or $Rh_3(CNR)_{12}I_2^{3+}$ both of which have metal-metal-bonded structures.[12-14] The factors which distinguish between halo-bridged and metal-metal-bonded structures in reactions of these types may relate to the intrinsic lability of the M-X bonds and they warrent further attention.

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