Table I. Summary of the Kinetic Data for the Reactions

$$[(\text{cod})\text{Ir}(\text{phen})]^+ + \text{CH}_3\text{I} \xrightarrow[\mu=0.01]{[\text{I}^-]} [(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{X} \ (\text{X} = \text{Cl, I})$$

$[\text{CH}_3\text{I}]$, mol·dm^{-3}	temp, °C	$[\text{I}^-]$, mol·dm^{-3}	$10^4 \times k_{\text{obsd}}$, s^{-1}	k_1, dm^3·mol^{-1} s^{-1}	k_2, dm^3·mol^{-1} s^{-1}
1.585	30	0.00	2.23	1.41×10^{-4}	
1.270			1.76	1.39×10^{-4}	
0.793			1.11	1.40×10^{-4}	
1.585	35		3.21	2.03×10^{-4}	
1.270			2.60	2.02×10^{-4}	
0.793			1.58	1.99×10^{-4}	
1.585	20		1.07	6.75×10^{-5}	
1.270			0.89	7.01×10^{-5}	
0.793			0.64	8.07×10^{-5}	
1.585	30	0.50	13.36		8.43×10^{-4}
1.270			10.63		8.37×10^{-4}
0.951			7.95		8.36×10^{-4}
1.585	35		17.82		1.12×10^{-3}
1.270			14.39		1.13×10^{-3}
0.793			9.28		1.17×10^{-3}
0.951			10.69		1.12×10^{-3}
1.585	20		7.13		4.50×10^{-4}
1.270			5.66		4.46×10^{-4}
0.793			3.51		4.43×10^{-4}

constant of methyl iodide attack on the four-coordinate $[(\text{cod})\text{Ir}(\text{phen})]^+\text{Cl}^-$. When the iodide concentration is taken to 0.50 mol·dm^{-3}, the only species in solution is the five-coordinated (cod)Ir(phen)I, so that rate law 3 becomes $k_{\text{obsd}} = k_2[\text{CH}_3\text{I}]$. These values of k_2 are given in Table II.

Scheme I

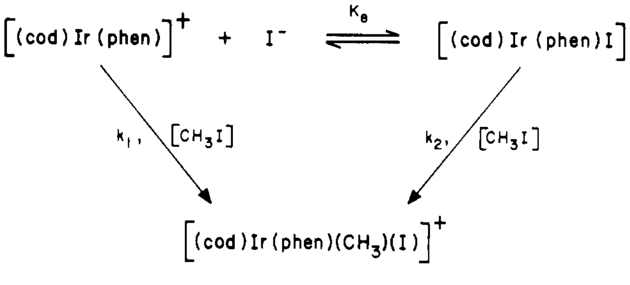

Table II. Summary of the Rate and Equilibrium Constants and Activation Parameters for the Reaction (25 °C)

$$[(\text{cod})\text{Ir}(\text{phen})]^+ + \text{CH}_3\text{I} \xrightarrow[\mu = 0.01]{[\text{I}^-]} [(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{X} \ (\text{X} = \text{Cl, I})$$

	k_1, dm^3·mol^{-1}·s^{-1}	k_2, dm^3·mol^{-1}·s^{-1}	K_e, dm^3·mol^{-1}
	$(9.1 \pm 0.8) \times 10^{-5}$ [a]	$(6.5 \pm 0.1) \times 10^{-4}$ [a]	235 ± 15[a]
	$(9.2 \pm 0.2) \times 10^{-5}$ [b]	$(6.4 \pm 0.1) \times 10^{-4}$ [b]	227 ± 5[c]
$\Delta H^\ddagger$, kJ·mol^{-1}	51.9 ± 0.4	44.7 ± 1.7	
$\Delta S^\ddagger$, kJ·mol^{-1}·deg^{-1}	−146 ± 4	−159 ± 4	

[a] Values obtained by using the SPSS program with rate law 3 as model. [b] Values obtained for $[\text{I}^-] = 0$ (k_1) and $[\text{I}^-] = 0.5$ mol·dm^{-1} (k_2). [c] Determined spectrophotometrically.

With use of all the data obtained at 25 °C, the rate and equilibrium constants were also obtained by using rate law 3 as the model in the SPSS nonlinear least-squares fit program[6] (Table II). From Table II it can be seen that good agreement was obtained between the k_1 and k_2 values obtained by experiment and by using the SPSS program. Also, the K_e values are in very good agreement.

The entropies of activation (Table II) are expectedly quite negative for reactions involving charged reactants and products and suggest a marked increase in polarity, or unusually stringent stereochemical restrictions, in going from reactants to the transition state. It is therefore reasonable to assume a transition-state configuration in which the iodide on the methyl group undergoes nucleophilic substitution by the iridium complex.

From the above data it is clear that oxidative addition of methyl iodide to the cationic $[\text{Ir}(\text{phen})(\text{cod})]^+\text{Cl}^-$ complex can proceed by two reaction mechanisms, i.e., either by electrophilic attack by the methyl group (followed by coordination of iodide) or by coordination of iodide (followed by methylation). Our results show unequivocably that the second path is preferred and consequently offers an explanation for iodide-catalyzed MeI oxidative-addition reactions.[1]

Experimental Section

Materials. Analytical grade methanol (Merck), distilled over magnesium and stored and transferred under nitrogen, was used for all the kinetic measurements.

The complexes Ir(cod)(phen)X (X = Cl, I) were prepared by published procedures,[7] and their reaction products with methyl iodide were characterized by microanalyses. Anal. Calcd for $[(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{Cl}$: C, 37.4; H, 3.1; N, 4.36; I, 19.7; Cl, 5.5. Found: C, 37.3; H, 3.2; N, 4.5; I, 20.1; Cl, 5.7. Anal. Calcd for $[(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{I}$: C, 32.7; H, 2.7; N, 3.8; I, 34.6. Found: C, 32.5; H, 2.9; N, 4.1; I, 35.0. Analytical grade sodium iodide and lithium chloride and reagent grade methyl iodide were obtained from Merck. Sodium iodide and lithium chloride were deaerated, dehydrated, and stored under nitrogen. Methyl iodide was extracted with aqueous sodium thiosulfate (to remove iodine), distilled under nitrogen, and stored over clean mercury. Purified nitrogen was supplied by the African Oxygen Co.

Kinetics. Electronic absorption spectra were measured and the reactions were followed on a Cary 15 spectrophotometer with a thermostated cell compartment, at temperatures of (20, 25, 30, 35) ± 0.1 °C. Pseudo-first-order conditions were maintained by ensuring that the concentrations of the methyl iodide were at least a factor of 30 greater than that of the starting complexes.

The reactions were followed at λ 550 nm, which corresponds to studying the rate of disappearance of the starting complex. Data were obtained at iodide concentrations (1, 2, 3, 5, 10, 500) × 10^{-3} mol·dm^{-3}. The ionic strength was kept constant with lithium chloride at $\mu = 0.01$.

The final UV–vis spectra of the reaction solutions were compared with those obtained from the prepared products and found to be identical. Also, the UV–vis spectra of $[(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{X}$ (X = Cl, I) were found to be identical.

Registry No. [Ir(cod)(phen)]Cl, 53522-11-5; [Ir(cod)(phen)]I, 80048-97-1; CH_3I, 74-88-4; $[(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{Cl}$, 80041-65-2; $[(\text{cod})\text{Ir}(\text{phen})(\text{CH}_3)(\text{I})]\text{I}$, 80041-66-3.

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(6) Nie, N. H.; Hull, C. H.; Jenkins, J. G.; Steinbrenner, K.; Bert, D. H. "Statistical Package for Social Sciences", 2nd ed.; McGraw-Hill: New York, 1975.

(7) Mestroni, G.; Camus, A.; Zassinovich, G. *J. Organomet. Chem.*, **1974**, *73*, 119.

Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Electron Paramagnetic Resonance Study of Nitrogen-Bridged Iron Porphyrin Dimers

Lawrence A. Bottomley* and Barry B. Garrett

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The determination of the physicochemical properties of μ-nitrido-bis[(5,10,15,20-tetraphenylporphinato)iron], $[(\text{TPP})\text{Fe}]_2\text{N}$, has been actively pursued,[1-7] as this is the first

Table I. Comparison of EPR Results as a Function of Solvent for $[(TPP)Fe]_2N$ at 77 K

solvent	g_x	g_y	g_z	$A_x{}^a$	$A_y{}^a$	$A_z{}^a$
toluene[b]	2.1582	2.1440	2.0082	22.27 (67.27)	22.25 (66.77)	23.54 (66.16)
toluene[b] containing 3.48 equiv of pyridine	1.9971	2.0051	2.0573			
1,2-dichloroethane		2.160	2.004	20.8_5 (63.0)		23.1 (65.0)
benzonitrile		2.157	2.008	21.9_5 (66.3)		23.0 (64.6)
carbon disulfide[c]		2.15	2.01	22		

[a] Hyperfine coupling constants are reported in gauss with values converted to MHz in parentheses: A_i (Hz) = $[A_i\ (G)](g_i\beta/h)$. [b] Measurements were made at both Q and X band. [c] Taken from ref 2.

example of two first-row transition metals being bridged by a single nitrogen atom. The combined efforts of a number of groups have sought to define the chemical reactivity of the parent complex as well as its redox products. Conflicting views[2-5] of the valence and spin states of each Fe atom have resulted. Mössbauer[1] and resonance Raman[2] spectra have been interpreted as indicative of two high-spin Fe(III) atoms in the dimer. On the other hand, X-ray studies[5] have shown that $[(TPP)Fe]_2N$ has equivalent iron atoms only 0.32 Å out of the porphyrin plane, a distance more consistent with a low-spin environment. Magnetic susceptibility values[1,6] of 2.04–2.08 μ_B are consistent with one unpaired electron per dimer. X-ray photoelectron spectroscopic data[3] unequivocally demonstrate that the iron atoms are equivalent. Molecular orbital calculations have subsequently predicted that both iron atoms should be equivalent and that the ground state of the dimer is $S = {}^1/_2$.[4]

In this note, we report results of X-band and Q-band EPR studies on $[(TPP)Fe]_2N$ in solutions and glasses of several solvents. From the observed spectra, the symmetry of the ground state is readily assigned as A_1, and the predicted low-spin assignment is confirmed. Hyperfine data allow a semiquantitative description of the spin distribution[8,9] between the iron atoms and the nitrogen bridge. Axial ligation of the dimer is observed in the glass matrices used to observe anisotropic EPR spectra. These ligated species have strong EPR lines near $g = 2$ that can obscure the parallel spectrum of the unligated dimer, even when the ligand is present only at impurity levels in the solvent.[2]

Experimental Section

$[(TPP)Fe]_2N$ was synthesized by thermal decomposition $[(TPP)Fe]_2N$ $(TPP)FeN_3$ in xylene as described by Summerville and Cohen.[1] 1,2-Dichloroethane was obtained from J. T. Baker as reagent grade. Aliquots were extracted with equal volumes of H_2SO_4 and H_2O, followed by distillation from P_2O_5 under N_2, and stored over 3-Å molecular sieves prior to use. Benzonitrile was obtained from Eastman Chemical and was distilled from P_{O5} under N_2 prior to use. Toluene and carbon disulfide were P_2O_5 grade and were used as received from Mallinckrodt. Pyridine, obtained from Scientific Products, was first shaken over KOH pellets, then distilled under N_2 from CaO, and stored over 3-Å molecular sieves.

All samples were 1 mg/mL in $[(TPP)Fe]_2N$ and were thoroughly degassed via three freeze–pump–thaw cycles prior to acquisition of spectra. Additions of pyridine were made directly in the EPR tube with Hamilton microsyringes. Mixing was performed in the liquid phase. EPR spectra were taken on a Varian E12 spectrometer at 9 and 35 GHz. Line positions were measured with a Spectromagnetic Industries Model 5200 NMR gauss meter and were reproducible to within ±0.1 G or better, depending on the line shape. Pitch (g = 2.0028) was used as an external standard to calibrate the microwave frequency.

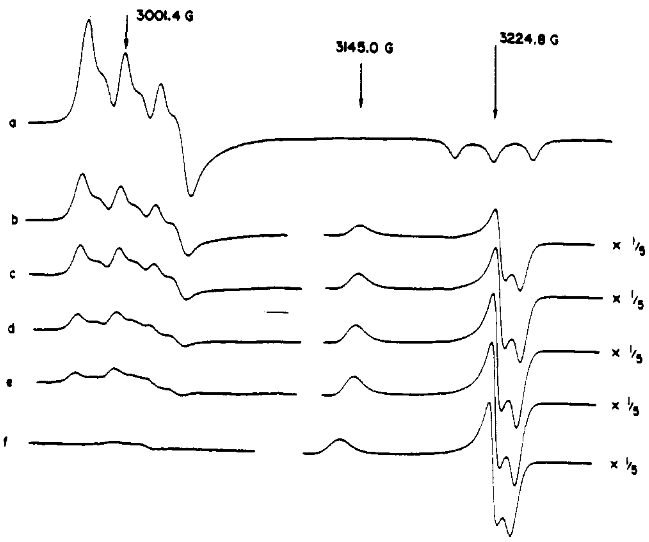

Figure 1. X-band (9.065-GHz) EPR spectra of 1.0 mg/mL $[(TPP)Fe]_2N$ samples frozen in toluene containing pyridine in the following relative amounts: (a) 0.0, (b) 0.87, (c) 1.74, (d) 2.61, (e) 3.48, (f) 4150 equiv.

Results and Discussion

The X-band spectrum of a 1.0 mg/mL sample of $[(TPP)Fe]_2N$ in a frozen toluene matrix at 77 K is depicted in Figure 1a. This spectrum contains lines corresponding to three different g factors with nitrogen hyperfine triplets for each. ESR lines were found in the g = 2 region with no evidence for resonances in the g = 4–6 region, which should appear for $S > {}^1/_2$ species. The high-field lines with g_z = 2.0082 and A_z = 23.54 G can be assigned to orientations with the magnetic field near the Fe–N–Fe axis because of the near-axial symmetry of the spectrum. The low-field peaks with g_x = 2.1582 and A_x = 22.27 G have higher field shoulders representing a distinct y-axis spectrum. The low-field, perpendicular region is completely resolved at Q-band, giving g_y = 2.1440 and A_y = 22.25 G. This rhombic spectrum implies that $[(TPP)Fe]_2N$ is distorted below axial symmetry in toluene glass. The anisotropy of the hyperfine interaction is reduced but not eliminated when A is transformed to g factor independent energy units (Table I). This anisotropy is of a different sign for dichloroethane glass than for toluene or benzonitrile, suggesting that the anisotropy is solvent induced and not a molecular property. In any case, this magnitude of anisotropy corresponds to less than 1% nitrogen p-orbital character.

The $[(TPP)Fe]_2N$ spectrum observed in toluene glass is similar to the one recently reported by Schick and Bocian[2] for a CS_2 glass, excepted that their g = 2 region contains a distorted doublet rather than the expected triplet. We have seen

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(1) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747–1752.
(2) Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 7984–7985.
(3) Kadish, K. M.; Bottomley, L. A.; Brace, J. G.; Winograd, N. *J. Am. Chem. Soc.* **1980**, *102*, 4341–4344.
(4) (a) Tatsumi, K.; Hoffmann, R.; Whangbo, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 509–511. (b) Tatsumi, K.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328–3341.
(5) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623–6628.
(6) Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. *Inorg. Chem.* **1981**, *20*, 3195–3200.
(7) Kadish, K. M.; Cheng, J. S.; Cohen, I. A.; Summerville, D. A. *ACS Symp. Ser.* **1977**, *No. 38*, Chapter 5.
(8) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–362.
(9) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; Chapter 9.

the same spectrum in CS_2 glass and believe the $g = 2$ region is obscured by a second spectrum arising from axial ligation by impurities in the solvent. Similar spectra were also observed in slightly impure THF, benzonitrile, and 1,2-dichloroethane. The obscuring spectra are like the high-field region of Figure 1b, which was obtained by adding pyridine to the toluene solvent system. The spectral features of the axially ligated species are clearly recognizable in the published CS_2 glass spectrum[2] once the shape is known. Careful solvent and sample preparation yields glassy spectra like Figure 1a with 1,2-dichloroethane, benzonitrile, and carbon disulfide (although not so well resolved as for toluene). Evidence for rhombic distortion can be seen in the g_x, g_y region of the spectra in each of these glasses. Rhombic distortions are also manifest in the nitrogen hyperfine anisotropy, which we have been able to measure accurately for three systems (see Table I). The fact that this anisotropy differs significantly in toluene and benzonitrile and is of the opposite sign in dichloroethane suggests that these rhombic distortions are imposed on the complex by the solvent glass and do not reflect internal electronically driven distortions for $[(TPP)Fe]_2N$. Even so, the consistent appearance of such distortions implies that the complex is rather flexible (in agreement with potential energy calculations by Tatsumi and Hoffmann[4]). Thus, we can estimate the spin-Hamiltonian parameters for the axially symmetric complex by averaging our most precise data (in toluene glass) to give $g_z = 2.0082$, $g_{x,y} = 2.1511$, and $A_{iso} = 66.7$ MHz. In solution, the g factor should be 2.103.

The nature of the second spectrum in the $g = 2$ region was clearly demonstrated by a titration experiment in which pyridine was added as a potential ligand. Figure 1 depicts the change in the EPR spectrum of $[(TPP)Fe]_2N$ as the relative pyridine concentration is increased from 0.87 (Figure 1b) to 4.15×10^3 equiv (Figure 1f). The original spectrum near $g = 2.15$ falls into the base line with a concomitant rise in signal near the free electron g value as the pyridine concentration is increased. The amplitudes of the three new lines ($g_x = 1.9971$, $g_y = 2.0051$, and $g_z = 2.0573$) are many times larger than those of the original complex because the spectrum is spread over a smaller magnetic field range. A log–log plot of the ratio of amplitudes for the signal at $g = 2.05$ (3145 G) to that for the lowest field component of the $g = 2.15$ region (2979 G) vs. pyridine concentration is linear with a slope of 0.96, indicating the formation of a monoadduct. The apparent formation constant for this adduct is 10^6 in the glass at 90 K. Addition of a large excess (greater than 5000 equiv) of pyridine results in growth of new lines in the $g = 2.15$ region, but the latter are complicated by the change of the solvent system. We suggest that the spectrum of the monopyridine adduct is characteristic of axial ligation and that such complexation is responsible for the distorted $g = 2$ regions for impure solvent glasses.

Previous optical,[1] NMR,[6] and electrochemical[6] investigations at ambient temperatures showed no evidence of coordination by nitrogen or oxygen donors at the vacant axial Fe sites of $[(TPP)Fe]_2N$. This apparent contradiction with the glass EPR data was resolved by examining the solution EPR spectra of a toluene solution containing pyridine and $[(TPP)Fe]_2N$ in 31 to 1 mole ratio. The room-temperature spectrum consists of a single 130 G wide line at $g = 2.117$. The line narrows slightly on cooling in the range from 50 by a −48 °C with no change in g factor. At lower temperatures precipitation is indicated by the development of a spectrum characteristic of the pure solid.[1] Samples with as much as 10^3 mole ratio of pyridine to $[(TPP)Fe]_2N$ give identical spectra with those obtained in pure toluene or 1,2-dichloroethane solvents. Formation of a pyridine adduct in solution would have been indicated by a shift of the average g factor toward $g = 2$ for rapid exchange or by the development of a new spectrum near 2.02 with slow exchange. We found no evidence for axial ligation by pyridine in the liquid phase. It is also notable that the solution $g = 2.117$ is significantly larger than the average $g = 2.103$ obtained from the toluene glass. This comparison suggests that there may be a small electronic rearrangement associated with the distortion that occurs in the glass.

The hyperfine parameters for $[(TPP)Fe]_2N$ indicate a significant amount of nitrido s character (4.2%) with essentially no nitrido p character. This situation corresponds to a molecule with D_{4d} symmetry in solution.[8,9] The large shift of g_x and g_y from the free electron value indicates that the majority of the spin density resides in a symmetric combination of d_{z^2} orbitals on the iron atoms; the small shift of g_z must arise from delocalization of some spin density onto the porphyrin ligands. This description of the spin density requires an A_1 ground state and may be compared with Hoffmann's prediction[4] of such a ground state with orbital populations: 44.5% on each iron d_{z^2}, 1.6% nitrido 2s, and the remaining 9.4% delocalized onto the porphyrin rings.

The complete change of EPR spectrum on complexation indicates a change of ground state. The unpaired electron is forced from the d_{z^2} orbital. The relative magnitude of the g shifts with only the unique axis component having a significant orbital contribution places the unpaired electron in either the $d_{x^2-y^2}$ or d_{xy} orbital. Any interaction other than axial ligation will tend to destabilize both $d_{x^2-y^2}$ and d_{xy} relative to d_{z^2}, which is contrary to the observations. The lack of axial symmetry is not as readily dismissed as for the parent compound because the difference between the x and y components of the g tensor is larger than their shifts from the free electron value. The resonance lines are narrow enough to reveal any hyperfine splitting in excess of 2.5 G (~7 MHz), thereby limiting nitrogen spin densities to $f_s < 0.45\%$ or $f_p < 7.3\%$. However, these limits are insufficient to differentiate between the two possible d-orbital ground states.

Upon pyridine complexation at the axial site, the ligated iron atom should be pulled near the porphyrin plane,[10] resulting in an increase in the ligand field about the metal and localizing the unpaired electron on the other metal center. This would give a six-coordinate Fe(IV) center and a low-spin, five-coordinate Fe(III) center. Retention of axial symmetry about Fe(III) would give a Jahn–Teller-sensitive orbital-doublet ground state $\{(xy)^2[(xz)^2(yz)^1](x^2 - y^2)^0(z^2)^0\}$. A distortion that destabilizes one of the degenerate orbitals $[(xz)(yz)]$ above the $d_{x^2-y^2}$ orbital (such as canting the Fe(III) porphyrin plane) would provide a ground state $[(xy)^2(xz)^2(x^2 - y^2)^1(yz)^0(z^2)^0]$, consistent with all aspects of the EPR spectrum. If such a large distortion is necessary to stabilize the electronic system of the adduct, then this may account for its failure to form in solution. While a suitable symmetry ground state could arise with the unpaired electron on the six-coordinate center with a weak axial ligand field, both of these conditions are contrary to expectation.[11] The preferred description places the unpaired electron on the five-coordinate center.

It is interesting to note the EPR spectrum of $\{(TPP)Fe]_2N\}\cdot C_5H_5N$ is similar to that reported[12,13] for the isoelectronic $\{[(TPP)Fe]_2O\}^+$ complex ($g_\parallel = 2.059$, $g_\perp = 1.993$), suggesting that these two species have similar electronic ground states. This comparison indicates the need for a reexamination of the EPR spectrum of $\{[(TPP)Fe]_2O\}^+$ and its sensitivity to axial ligation. $[(TPP)Fe]_2N$ was seen to interact with im-

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(10) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339–345.

(11) Palmer, G. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, Chapter 6.

(12) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 504–514.

(13) Felton, R. H.; Owen, G. S.; Dolphin, D.; Fajer, J. *J. Am. Chem. Soc.* **1971**, *93*, 6332–6334.

purities in every solvent we have used. This suggests that complexation of $[(TPP)Fe]_2N$ with a variety of Lewis bases can be used to probe the coordination chemistry of Fe(IV). We also have evidence for interaction of a second ligand with the dimer at very high concentrations of pyridine. The attachment of a second ligand should reestablish symmetry in the system, giving access to other features of the molecular orbital ordering in these binuclear systems.

In summary, this work has unequivocally demonstrated that $[(TPP)Fe]_2N$ has an A_1 ground state with two equivalent, low-spin iron centers. Complexation by pyridine or other Lewis bases yields an unsymmetrically substituted dimer, which is further distorted below axial symmetry. The adduct remains low spin with the unpaired electron assigned to the Fe(III) center in a $d_{x^2-y^2}$ orbital.

Registry No. $[(TPP)Fe]_2N$, 59114-43-1; pyridine, 110-86-1.

Contribution from the Frank J. Seiler Research Laboratory,
USAF Academy, Colorado 80840,
and Department of Chemistry, University of Mississippi,
University, Mississippi 38677

Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-Temperature Ionic Liquids for Electrochemistry, Spectroscopy, and Synthesis

John S. Wilkes,* Joseph A. Levisky, Robert A. Wilson, and Charles L. Hussey

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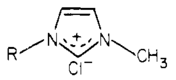
Fused salts that are liquid at room temperature are an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organometallic, and organic solutes. In addition, these ionic liquids are potentially useful as electrolytes in batteries, photoelectrochemical cells, and electroplating. In recent years some mixtures of aluminum chloride and 1-alkylpyridinium chlorides have been reported to be molten at or near room temperature. Melts of this type may be prepared easily,[1] and one example (aluminum chloride/1-butylpyridinium chloride) has been extensively studied.[2-4] One very attractive feature of this system is the wide range of Lewis acidity attainable, as expressed by chloride concentration.[5]

Gale and Osteryoung pointed out that potential measurements at an aluminum electrode in basic mixtures of $AlCl_3$ and 1-butylpyridinium chloride (i.e., less than 1:1 mole ratio) were unreliable due to apparent reaction of aluminum with the melt.[5] They later showed that the 1-butylpyridinium cation was reduced by aluminum in that melt.[6] This reduction of the cation foreshortens the electrochemical window of the basic chloroaluminate melts. The term electrochemical window is used here as the difference between the anodic and cathodic decomposition potentials, in volts, for the melt. Also, none of the 1-alkylpyridinium chloroaluminate melts are liquid at room temperature over the entire available acidity range. We report here the preparation and properties of a new chloroaluminate molten salt that is also liquid at room temperature but has improved electrochemical and physical properties.

Table I. Conductivities of Methylethylimidazolium Chloroaluminate Melts

compn, mol % $AlCl_3$	κ,[a] Ω^{-1} cm^{-1}	temp, °C	compn, mol % $AlCl_3$	κ,[a] Ω^{-1} cm^{-1}	temp, °C
44	0.0117	29.7	67	0.0154	32.2
50	0.0227	30.9			

[a] Specific conductivity.



I, R = methyl
II, R = ethyl
III, R = propyl
IV, R = butyl

While many organic cations would probably have sufficient size to produce low melting chloroaluminate salts, the cations must also have reduction potentials more negative than Al(III) in the melts in order to be unreactive toward Al and to improve the electrochemical window. Using Dewar's MNDO technique,[7] we calculated the electron affinities of a variety of organic cations as a screen for species that would be less easily reduced than 1-alkylpyridinium ions. The 1,3-dialkylimidazolium salts were revealed as attractive candidates since their reduction potentials were predicted to be about 0.8 V lower than the 1-alkylpyridinium salts, and they could be prepared readily from commercially available starting materials. A homologous series of 1,3-dialkylimidazolium chlorides (compounds I–V) were prepared and properties of mixtures of these salts with aluminum chloride were studied.[8] The chloroaluminate melt prepared from one of the chlorides, 1-methyl-3-ethylimidazolium chloride (MeEtImCl), had the most favorable physical and electrochemical properties and was one of the easiest to prepare. The properties that we report here for the melt indicate that it is superior to previous melts in terms of liquidus temperatures, electrochemical window, and reactivity with aluminum. It is similar to the earlier alkylpyridinium chloroaluminates in its conductivity, viscosity, wide range of Lewis acidity, and its ability to solvate both organic, organometallic, and inorganic compounds. For example, thianthrene, ferrocene, $CuCl_2$, and $TiCl_4$ are all soluble. The methylethylimidazolium chloroaluminate melts are miscible with benzene and toluene to about 50% (v/v) and miscible in all proportions with acetonitrile. The new melts and mixtures of them with benzene are suitable solvents for spectroscopic measurements. The 66 mol % melt and melt diluted with benzene (50% v/v) are both useful to ca. 320 nm. The 40 mol % $AlCl_3$ composition and that diluted with similar amounts of benzene are suitable for use to about 280 nm. The $MeEtImCl/AlCl_3$ mixtures are liquid at 25 °C over the range of composition from 40 to 67 mol % $AlCl_3$. The liquidus temperatures for 50 and 67 mol % melts were 8 and −98 °C, respectively, although the lower temperature may be a glass transition of a super-cooled liquid. The low melting point of

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*To whom correspondence should be addressed at the USAF Academy.

(1) H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **97**, 3264 (1975).
(2) R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi, and C. L. Hussey, *J. Electrochem. Soc.*, **126**, 1644 (1979).
(3) C. L. Hussey, L. A. King, and R. A. Carpio, *J. Electrochem. Soc.*, **126**, 1029 (1979).
(4) C. L. Hussey, L. A. King, and J. S. Wilkes, *J. Electroanal. Chem. Interfacial Electrochem.*, **102**, 321 (1979).
(5) R. J. Gale and R. A. Osteryoung, *Inorg. Chem.*, **18**, 1603 (1979).
(6) R. J. Gale and R. A. Osteryoung, *J. Electrochem. Soc.*, **127**, 2167 (1980).
(7) M. Dewar, H. Kollmar, and S. Suck, *Theor. Chim. Acta*, **36**, 237 (1975).
(8) J. S. Wilkes, J. A. Levisky, C. L. Hussey, and M. L. Druelinger, *Proc. Int. Symp. Molten Salts*, **81-9**, 245–255 (1980).