Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science, Calcutta 700 032, India

Bis(2-(phenylazo)pyridine)copper(I) and -copper(II): Ligand π Acidity and High Formal Potential of the Copper(II)-Copper(I) Couple

DIPANKAR DATTA and ANIMESH CHAKRAVORTY*

Received August 2, 1982

2-(Phenylazo)pyridine (L) yields cationic bisligand complexes with both copper(II) and copper(I). These are isolated as the perchlorates $[CuL_2](ClO_4)_2$ and $[CuL_2]ClO_4$. Grossly planar and tetrahedral structures are assigned to CuL_2^{2+} and CuL_2^+, respectively. The N=N stretch in CuL_2^+ shows a large shift to lower frequency (1375 cm^{-1}) from the free-ligand value due to d(Cu)-π^*(L) back-bonding. This effect is much less pronounced in CuL_2^{2+}. The copper(I) complex shows two allowed transitions in the visible region tentatively assigned to $t_2 \rightarrow \pi^*$ (700 nm) and $e \rightarrow \pi^*$ (560 nm) charge transfer. A broad ligand field band occurs in CuL_2^{2+} at 606 nm in MeCN. In the same solvent CuL_2^+ undergoes solvolytic equilibria, resulting in a decrease in extinction coefficient of the 700-nm band with dilution. The equilibrium constants for the reactions

$$CuL_2^+ \overset{K_1}{\rightleftharpoons} CuL^+ + L \qquad CuL^+ \overset{K_2}{\rightleftharpoons} Cu^+ + L$$

are (298 K) $K_1 = 0.83 \times 10^{-3}$ M^{-1} and $K_2 = 1.00 \times 10^{-3}$ M^{-1}. In methanol the couple CuL_2^{2+}-CuL_2^+ has a formal potential, E°_{298}, of 0.630 V at 298 K (voltammetry at platinum). The high potential is brought about by the strong d(Cu)-π^*(L) bonding. Electrochemical studies in acetonitrile show that the solvolytic equilibria noted above are coupled with the electron-transfer step. The results can be rationalized by considering the observed response to be a weighted average of those due to the couples CuL_2^{2+}-CuL_2^+ (E°_{298} = 0.735 V), CuL_2^+-CuL^+, L (0.533 V), and CuL_2^{2+}-Cu^+, 2L (0.376 V).

Introduction

The CuN_4 coordination sphere is a familiar feature in copper chemistry. Quite generally the stereochemical requirements of copper(I) and copper(II) are different.[1] The redox couple (eq 1) may thus be expected to be stereodynamic and to lack

$$Cu^{II}N_4 + e^- \rightleftharpoons Cu^IN_4 \qquad (1)$$

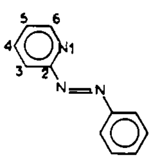
electrochemical reversibility to that extent. On the other hand, it should be possible to control the potential of the couple by tailoring steric requirements of associated ligands. Thus the planarity of some nitrogen macrocycles is more compatible with copper(II) than with copper(I) and the formal potentials of couple 1 in such complexes are accordingly low, usually occurring[2-5] on the negative side of the saturated calomel electrode (SCE). In contrast, some bis complexes of substituted 2,2′-bipyridine (bpy) and related ligands have[6-8] high[9] potentials as a result of substituent steric hindrance that favors[10] pseudotetrahedral N_4 geometry, hence Cu^IN_4. Recently a high-potential system has been designed with utilization of steric and hydrophobicity characters of tripod ligands.[11] The total number of high-potential CuN_4 species known to date is still surprisingly small. Current interest in high-potential copper complexes arises from their biological relevance.[12]

Herein we report an approach toward high-potential CuN_4 systems using an electronic control via ligand π acidity which preferentially stabilizes as the lower oxidation state; the ligand[13,14] concerned is 2-(phenylazo)pyridine (L, **1**). In ruthenium complexes[15-18] of L, the metal(III)-metal(II) couple

Table I. Some Physical Properties of the Complexes

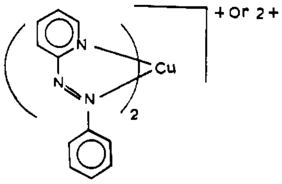
measmt	$[CuL_2](ClO_4)_2$	$[CuL_2]ClO_4$
1. soln conductivity Λ_M, Ω^{-1} cm^2 M^{-1}	234,[a] 151[b]	168,[a] 96[b]
2. magnetic moment μ, μ_B	1.83[c]	diamagnetic
3. IR spectra,[d] cm^{-1}	1600,[e] 1580,[e] 1470,[e] 1448,[e] 1412,[f] 778,[g] 680,[h] 1080,[i,j] 615[k]	1585,[e] 1465,[e] 1440,[e] 1375,[f] 782,[g] 678,[h] 1080,[i,j] 620[k]
4. electronic spectra[l] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	606 (123), 332 (22 700), 224 (19 900)	700 (1600), 560 (6800), 354 (37 800), 230 (24 300)

[a] The solvent was MeCN. Concentrations are as follows: $[CuL_2](ClO_4)_2$, 1.855×10^{-3} M; $[CuL_2]ClO_4$, 1.841×10^{-3} M. [b] The solvent was MeOH. Concentrations are as follows: $[CuL_2](ClO_4)_2$, 1.644×10^{-3} M; $[CuL_2]ClO_4$, 1.830×10^{-3} M. [c] At room temperature, 297.5 K. [d] In KBr disk; all bands are of strong or medium intensity. [e] $\nu_{C=C} + \nu_{C=N}$. [f] $\nu_{N=N}$. [g] $\delta_{C-H}(NC_5H_4)$. [h] $\delta_{C-H}(C_6H_5)$. [i] ν_3 of ClO_4^-. [j] Center of a very broad band. [k] ν_2 of ClO_4^-. [l] Solvents are as follows: $[CuL_2](ClO_4)_2$, MeCN; $[CuL_2]ClO_4$, MeOH.



(L)

1



2

---

(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 798.

(2) Tokel, N. E.; Katovic, V.; Farmery, K.; Anderson, C. B.; Busch, D.H. *J. Am. Chem. Soc.* **1970**, *92*, 400. Rillema, D. P.; Endicott, J. F.; Papconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739. Olson, D. C.; Vasilevskis, J. *Ibid.* **1971**, *10*, 463.

(3) Gagnê, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170. Gagnê, R. R.; Allison, J. L.; Ingle, D. M. *Inorg. Chem.* **1979**, *18*, 2767.

(4) The increase of the potential with increased macroycle flexibility is documented.[5]

(5) Nickles, D. E.; Powers, M. J.; Urbach, F. L. *Inorg. Chim. Acta* **1979**, *37*, L499.

(6) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

(7) Nelson, I. V.; Iwamoto, R. T. *Anal. Chem.* **1963**, *35*, 867.

(8) Patterson, G. H.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

(9) In this work "high" is used to mean potentials greater than 0.5 V vs. SCE or 0.75 V vs. NHE.

(10) Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, *21*, 1881.

(11) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1981**, *20*, 1014.

(12) Malmstrom, B. G. In "New Trends in Bioinorganic Chemistry"; Williams, R. J. P., Da Silva, J. R. R. F., Eds.; Academic Press: New York, 1978; p 59.

(13) Raghavendra, B. S.; Chakravorty, A. *Indian J. Chem., Sect. A* **1976**, *14A*, 166.

(14) Campbell, N.; Henderson, A. W.; Taylor, D. *J. Chem. Soc.* **1953**, 1281.

(15) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 2246; **1982**, *21*, 2737.

(16) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *Inorg. Chem.*, in press, and unpublished results.

0020-1669/83/1322-1085$01.50/0

occurs at potentials much higher than those of the corresponding bpy complexes. This led us to anticipate that a similar situation could apply to other metal ions,[19] and we report here the synthesis, characterization, solution equilibria, and redox properties of the perchlorates of CuL_2^{2+} and CuL_2^+ (**2**). We note that some insoluble copper complexes of 2,2′-, 3,3′-, and 4,4′-azopyridine and their spectra are described in the literature.[20]

Results and Discussion

A. Synthesis. Reaction of **1** in acetonitrile with $Cu(ClO_4)_2{\cdot}6H_2O$ (eq 2) gives crystals of $[CuL_2](ClO_4)_2$, which have

$$Cu(ClO_4)_2{\cdot}6H_2O + 2L \rightarrow [CuL_2](ClO_4)_2 + 6H_2O \qquad (2)$$

a deep blue sheen. The powdered material is brownish yellow. The copper(II) complex is a potent oxidant and is slowly converted to the copper(I) form in the presence of moisture even in the solid state. This conversion in which water is oxidized[21] becomes facile in hot moist solvents. The synthesis of dark violet crystals of $[CuL_2]ClO_4$ utilizes this phenomenon in that the same reactants (eq 2) are simply boiled in aqueous methanol. Alternatively the synthesis is achieved by the reaction shown by eq 3 carried out under dinitrogen in acetonitrile.

$$[Cu(MeCN)_4]ClO_4 + 2L \rightarrow [CuL_2]ClO_4 + 4MeCN \qquad (3)$$

The copper(I) complex and its methanol solutions are stable indefinitely. Although reaction 3 is reversible, the equilibrium constant is large (vide infra) and this constitutes a practical synthesis.

The diamagnetic copper(I) complex is a 1:1 electrolyte in MeCN and MeOH while the paramagnetic ($\mu = 1.83\ \mu_B$) copper(II) complex is a 1:2 electrolyte (Table I).

B. Spectra and Structure. Selected infrared frequencies are in Table I. The very broad and structureless ν_3 band of ClO_4^- suggests[22] the lack of significant perchlorate coordination in the solid state as in the solution phase (conductivity data). The N═N stretching frequency in L is[13] 1425 cm^{-1}. This frequency is very considerably lowered in CuL_2^+ (1375 cm^{-1}) but not in CuL_2^{2+} (1412 cm^{-1}), which we attribute to the presence of extensive d(Cu)–π^*(L) back-bonding in the copper(I) complex. Here π^*(L) is the LUMO of the azo imine chromophore. The behavior of CuL_2^+ is similar to those[13,18] of FeL_3^{2+} ($\nu_{N=N}$ = 1355 cm^{-1}) and RuL_3^{2+} (1358 cm^{-1}), where extensive d–π^* bonding is present.[23,24] In CuL_2^{2+} as in NiL_3^{2+} ($\nu_{N=N}$ = 1428 cm^{-1}) this type of bonding is understandably[25,26] unimportant.

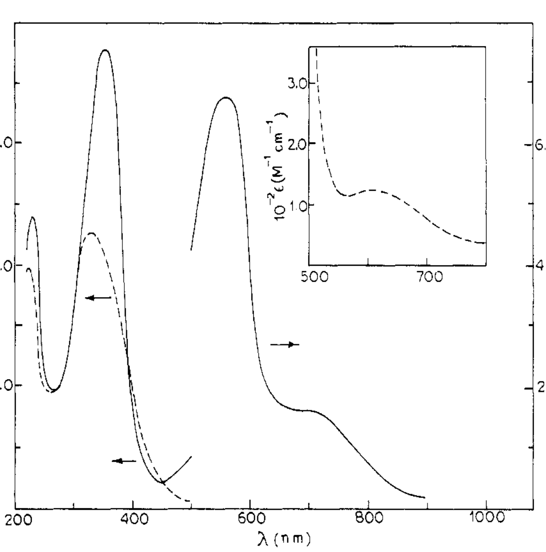


Figure 1. Electronic spectra of $[CuL_2](ClO_4)_2$ in MeCN (---) and $[CuL_2]ClO_4$ in MeOH (—).

A characteristic feature of complexes displaying sizable ground-state d–π^* bonding with conjugated organic chromophores is the frequent occurrence of low-energy metal-to-ligand charge-transfer transition(s) (MLCT) due to the d $\rightarrow$ π^* excitation. This is true[13,15–18] for iron(II) and ruthenium(II) complexes of L. The copper(I) complex falls in line (Figure 1, Table I) with two bands at 700 and 560 nm in methanol solution. These obey Beer's law, and hence the CuL_2^+ ion is stable in this solvent (this is not so in acetonitrile). That chelation of L occurs at pyridine and azo nitrogen atoms in the manner shown in **2** is documented in the known structures[23] of ruthenium complexes. It is reasonable[27–29] to assume that this copper(I) complex is grossly tetrahedral in the CuN_4 coordination sphere.

Some observations on the MLCT spectrum are in order. Octahedral NiL_3^{2+} displays a ligand field spectrum and has[13] a *Dq* of 1080 cm^{-1}. Hence in the hypothetical tetrahedral complex NiL_2^{2+}, *Dq* is estimated[30] to be ~500 cm^{-1}. Replacement of nickel by copper under the same gross geometry and oxidation state would change *Dq* only slightly. But in going to tetrahedral CuL_2^+, a pronounced decrease in *Dq* is expected due to a decrease of the metal oxidation number. We estimate the *Dq* of CuL_2^+ is roughly 50% of that of CuL_2^{2+}, i.e., ~300 cm^{-1}. The separation of t_2 and e orbitals in the hypothetical CuL_2^{2+} (tetrahedral) and in CuL_2^+ are therefore ~5000 and ~3000 cm^{-1}, respectively. If the two MLCT bands of CuL_2^+ are due to the transitions $t_2 \rightarrow \pi^*$ (700 nm) and $e \rightarrow \pi^*$ (560 nm), the energy gap between them should lie somewhere in the range 3000–5000 cm^{-1} since the excited states have considerable copper(II) character. The observed difference is 3600 cm^{-1}. A similar situation occurs[31] in the bis(arylazo oximates)[27–29] of copper(I). In bis complexes of copper(I) with bpy and related ligands the lowest energy charge-transfer band occurs[32] near 450 nm. In grossly planar and unsaturated macrocyclic environments for copper(I), an allowed transition is documented[3,33] near 700 nm.

---

(17) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600.

(18) Krause, R. A.; Krause, K. *Inorg. Chem.* **1982**, *21*, 1714.

(19) The formal potentials of iron(III)–iron(II) and nickel(II)–nickel(0) couples in FeL_3^{2+} and NiL_3^{2+} are respectively (in acetonitrile) 1.84 and −0.17 V vs. SCE (Goswami, S.; Bandyopadhyay, P.; Chakravorty, A., unpublished results).

(20) Baldwin, D. A.; Lever, A. B. P.; Parish, R. V. *Inorg. Chem.* **1969**, *8*, 107. Beadle, P. J.; Grazeskowiak, R.; Goldstein, M.; Goodgame, D. M. L. *J. Chem. Soc. A* **1970**, 305.

(21) The product(s) of this oxidation is (are) not yet known. We note that CuL_2^{2+} is smoothly reduced by aqueous hydrogen peroxide. The nature and mechanism of these important reactions are under investigation and will be published separately.

(22) Elder, R. C.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 427.

(23) In two isomers of $RuCl_2L_2$ the average Ru–N(azo) bond (1.98 Å) is shorter[23] than the average Ru–N(pyridine) bond (2.05 Å) (Ray, S.; Seal, A., private communication). The d–π^* bonding is thus substantially localized on the azo orbitals, hence the decrease in $\nu_{N=N}$ and the long N═N distance[23] (average 1.29 Å). This situation may also apply to CuL_2^+. In arylazooximates of palladium also there is good electrochemical evidence[24] that the LUMO is essentially an azo orbital.

(24) Bandyopadhyay, P.; Mascharak, P. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 675.

(25) Significant d–π^* bonding would proceed well in cases where a higher metal oxidation state is readily accessible as in the cases of Fe(II), Ru(II), and Cu(I). This does not apply[26] to Cu(II) and Ni(II).

(26) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.

(27) The structure of a tetrahedral copper(I) complex[28] of the azo imine chromophore, viz., Cu(MeC(NO)NNPh)(MeC(NOH)NHPh), is accurately known.[29]

(28) Gupta, S.; Kalia, K. C.; Chakravorty, A. *Inorg. Chem.* **1971**, *10*, 1534.

(29) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1980**, *19*, 3112.

(30) If the signs are ignored, $(Dq)_{tet} = {}^4/_9(Dq)_{oct}$.

(31) In the complex noted in ref 27 two allowed bands occur[28] at 770 and 580 nm. These are believed to be of the same origin as those in CuL_2^+ (Datta, D.; Chakravorty, A., to be submitted for publication).

(32) Kitagawa, S.; Munakata, M. *Inorg. Chem.* **1981**, *20*, 2261. Smith, G. F.; McCurdy, W. H., Jr. *Anal. Chem.* **1952**, *24*, 371.

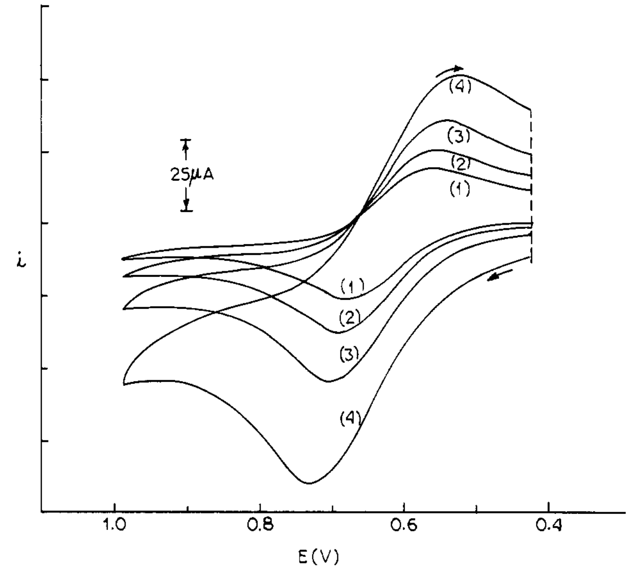


Figure 2. Cyclic voltammograms of $[CuL_2](ClO_4)_2$ (0.9601 × 10^{-3} M) in MeOH at various scan rates (mV s^{-1}): (1) 50; (2) 100; (3) 200; (4) 500.

In acetonitrile solution the electrolytic dissociation of $[CuL_2](ClO_4)_2$ is complete.[34,35] Unlike CuL_2^+, CuL_2^{2+} obeys Beer's law in acetonitrile.[36] In the latter complex a broad band occurs at 606 nm partly superimposed on a steeply rising absorption on the higher energy side (Figure 1). In view of its low intensity, the 606-nm band is assigned to d → d excitation. It is proposed that CuL_2^{2+} is grossly trans planar[37,38] with possible axial coordination by the solvent.

C. The Copper(II)-Copper(I) Couple. Since CuL_2^{2+} oxidizes water, it is evident that the redox couple (eq 4) has a

$$CuL_2^{2+} + e^- \rightleftharpoons CuL_2^+ \qquad (4)$$

high formal potential. The spectral evidence shows that d-π* bonding occurs preferentially in the copper(I) complex, which is thus stabilized. This is believed to be the dominant factor in making the potential of the couple (4) high. We wish to stress that in the trans-planar arrangement of L_2 the steric demand[39] for a changeover to tetrahedral geometry is small.

The formal potential ($E°_{298}(4)$) of couple 4 was determined with use of cyclic voltammetry with platinum as the working electrode. Methanol (0.1 M in tetraethylammonium perchlorate (TEAP)) was used as the solvent since both members of the couple are stable[40] in this medium. The electrochemical behavior in acetonitrile is complicated by solvolytic ligand dissociation in CuL_2^+ and is considered in a later section. All potentials reported in this work are referenced to the SCE.

Table II.[a,b] Cyclic Voltammetric Data for the Complexes in Methanol at 298 K

complex	v, V s^{-1}	E_{pa}, V	E_{pc}, V	ΔE_p, mV	$E°_{298}$, V
$[CuL_2](ClO_4)_2$	0.050	0.682	0.567	115	0.624
	0.100	0.695	0.555	140	0.625
	0.200	0.705	0.545	160	0.625
	0.500	0.735	0.525	210	0.630
$[CuL_2]ClO_4$	0.050	0.690	0.578	112	0.634
	0.100	0.700	0.568	132	0.634
	0.200	0.718	0.550	168	0.634
	0.500	0.740	0.530	210	0.635

[a] Meanings of the symbols used are the same as in the text; all E values are quoted vs. the SCE. [b] Coulometric data: 15.98 mg of $[CuL_2](ClO_4)_2$ electrolyzed at a platinum-wire gauge electrode in methanol at 0.0 V vs. SCE; Q(found), 2.30; Q(calcd), 2.45; $n = Q(\text{found})/Q(\text{calcd}) = 0.94$. The reduced solution was reoxidized at 0.800 V vs. SCE to give Q(found) = 2.35.

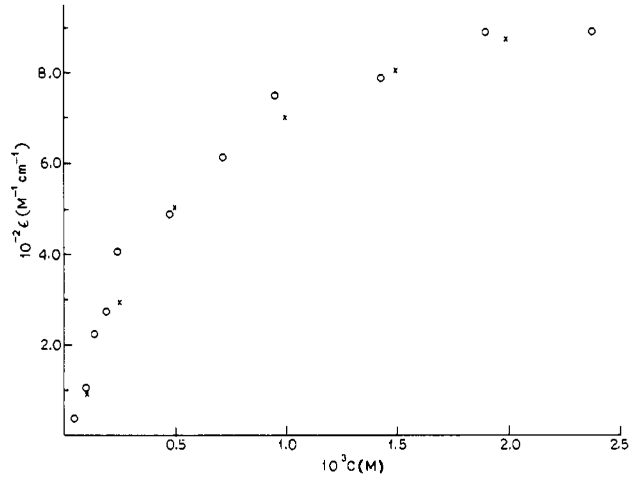


Figure 3. Variation of the extinction coefficient (ε) of a solution of $[CuL_2]ClO_4$ in MeCN with concentration (C): (O) experimental curve; (X) calculated curve.

A quasi-reversible one-electron response is displayed by $[CuL_2](ClO_4)_2$ on the positive side of the SCE. The separation, ΔE_p, between the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials increases with increase in scan rate (v) (Figure 2, Table II). From the observed ΔE_p values it is clear that the observed couple is quasi-reversible under the conditions of measurements. As expected, the variable-scan voltammograms of $[CuL_2]ClO_4$ differ only slightly (Table II) from those of the copper(II) analogue. The response under discussion is evidently due to couple 4. The one-electron stoichiometry is fully corroborated by coulometric data (Table II). The formal potential of the couple was computed as the average of E_{pa} and E_{pc}. The mean $E°_{298}$ value is 0.630 V. The quasi-reversible nature of couple 4 is a logical consequence of the stereochemical rearrangement (planar-tetrahedral) that accompnaies electron transfer.

Although high potentials are observed in sterically hindered substituted bipyridyl complexes,[6-8] the copper(II)-copper(I) couples in $Cu(py)_4^{2+}$ and $Cu(bpy)_2^{2+}$ have formal potentials of 0.05 and -0.13 V, respectively, in aqueous medium.[6] The formal potential of the azopyridine chelate system is thus much higher.[41] The role of the azo imine function in bringing about

---

(33) Katovic, D.; Taylor, L. T.; Urbach, F. L.; White, W. H.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 479.

(34) The cation $Cu(bpy)_2^{2+}$ readily associates[35] with anions (X^-), including ClO_4^-, to produce $Cu(bpy)_2X^+$. This situation is much less prevalent in the case of CuL_2^{2+}, which however does associate with halide ions. This phenomenon is under investigation.

(35) McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 135.

(36) The spectrum of $[CuL_2](ClO_4)_2$ was also examined in methanol. In this solvent a very small concentration of CuL_2^+ is invariably formed, possibly due to reduction of CuL_2^{2+} by an impurity. Even though the concentration of CuL_2^+ is slight, its intense bands in the visible region obscure observation of the weak ligand field spectrum of CuL_2^{2+}.

(37) The cis planar stereochemistry would be untenable[15] on steric grounds (proximity of the two phenyl rings). Pseudotetrahedral geometry for CuL_2^{2+} is rejected since in that case the presence of one or more ligand field bands near 5000 cm^{-1} would be anticipated (the estimated $(Dq)_{tet}$ is 500 cm^{-1}; see text). We note that planar bis chelates of copper(II) with oxygen and nitrogen ligands quite commonly display a broad ligand field band with or without resolved structure in the region 500-650 nm.[38]

(38) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.

(39) The pyridine ring 6-H of one L can have some interaction with the Ph group of the other L. The magnitude of this interaction is however small. This is also evident in the stability[15,17] of *trans*-$RuCl_2L_2$.

(40) The presence[36] of a slight amount of CuL_2^+ in solutions of CuL_2^{2+} in methanol in no way vitiates the electrochemical results.

(41) The change in medium from H_2O to MeOH cannot be responsible for the large difference. In fact, we have also measured[20] the potential of couple 4 in aqueous solution; the $E°_{298}$ value is 0.675 V, which is *higher* than that in methanol. Thus the difference in the potential of the bpy (or py) complex and that of the L complex is genuinely large.

a high copper(II)–copper(I) potential is conspicuously revealed by this comparison. We note that the ruthenium(III)–ruthenium(II) couple shifts[15,16,42] by 300 ± 100 mV for each replacement of bpy by L. The formal potentials of the copper(II)–copper(I) couple of $Cu(bpy)_2^{2+}$ and CuL_2^{2+} display a similar shift.

The electroactivity of CuL_2^{2+} and CuL_2^+ was examined only briefly at potentials negative to the SCE. A single multielectron (estimated to be 4e) quasi-reversible ($E_{pc} = -0.775$ V, $\Delta E_p = 310$ mV, $v = 50$ mV s^{-1}) cyclic response is observed for both the complexes. It is believed that this response arises from reduction of the two azo imine functions attended by protonation. As part of our studies on the behavior of CuL_2^{2+} and CuL_2^+ in aqueous medium, the pH dependence of the response is under investigation.[21,41] We note that in nonprotic media complexes of azo ligands are known to display successive 1e reduction steps for the azo function.[15,16,24]

D. Solvolysis of CuL_2^+ in Acetonitrile. (a) Equilibria. The high affinity of copper(I) for acetonitrile is well established.[43] It was therefore of interest to examine the stability of CuL_2^+ in this solvent. A measurable dissociation of CuL_2^+ was indeed found to occur in acetonitrile. This is indicated by the failure of CuL_2^+ to obey Beer's law in this solvent. The intensity of the band at 700 nm decreases progressively with dilution (Figure 3). On addition of L to the solution, the intensity again builds up, finally reaching a limiting value of 1340 M^{-1} cm^{-1} at high ligand concentrations. The results can be rationalized in terms of equilibria 5a and 6a, which have been

$$CuL_2^+ \overset{K_1}{\rightleftharpoons} CuL^+ + L \tag{5a}$$

$$K_1 = lrq^{-1} \tag{5b}$$

$$CuL^+ \overset{K_2}{\rightleftharpoons} Cu^+ + L \tag{6a}$$

$$K_2 = lsr^{-1} \tag{6b}$$

simplified by not showing explicitly the participation of acetonitrile (CuL^+ is probably $CuL(MeCN)_2^+$ while Cu^+ is[43] $Cu(MeCN)_4^+$). Here q, r, s, and l are respectively the equilibrium concentrations of CuL_2^+, CuL^+, Cu^+, and L.

The equilibrium constants K_1 and K_2 were determined with use of the intensity at 700 nm in solutions having varying concentrations of L at a constant copper concentration. The details of the determinations are given in the Experimental Section. It is assumed that the extinction coefficient of CuL_2^+ is twice that of CuL^+. This is reasonable.[45] The Cu^+ ion, i.e., $Cu(MeCN)_4^+$, is transparent in the visible region. The experimental values of K_1 and K_2 at 298 K are 0.83×10^{-3} and 1.00×10^{-3} M^{-1}. Interestingly K_2 is slightly larger than K_1. In effect the mixed complex CuL^+ is less stable than CuL_2^+ with respect to solvolytic displacement of L.

Given K_1 and K_2, the extinction coefficient of any given solution made by dissolving $[CuL_2]ClO_4$ in acetonitrile can be calculated. The good fit between calculated and experimental intensity patterns can be seen in Figure 3. We have not seen any previous report on the quantitative study of solvolytic equilibria of types 5 and 6 in acetonitrile. The irreversible displacement of ligand by acetonitrile occurs[46] in, e.g., the phenyldiazene complex of copper(I).

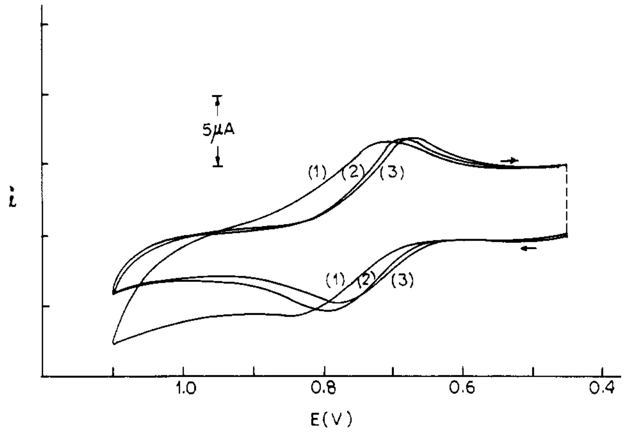


Figure 4. Cyclic voltammograms of a solution of $[CuL_2]ClO_4$ (0.1556×10^{-3} M) in MeCN at various concentrations (M) of externally added L: (1) 0.0000; (2) 0.5393×10^{-3}; (3) 1.5418×10^{-3}. The scan rate in each case is 50 mV s^{-1}.

(b) Effect on Redox Thermodynamics. A 1.56×10^{-4} M solution of CuL_2^+ in acetonitrile (0.1 M in TEAP) shows a quasi-reversible one-electron copper(II)–copper(I) response with an $\bar{E}_p$ of 0.775 V, where $\bar{E}_p$ is the average of anodic and cathodic potentials. On the addition of ligand the potential shifts to lower values (Figure 4). Thus with the concentration of externally added ligand at 2.6×10^{-3} M, $\bar{E}_p$ is 0.717 V. This shift in $\bar{E}_p$ can logically arise from the coupling of dissociation equilibria 5a and 6a with the electron-transfer equilibrium 4. Since CuL_2^{2+} is stable in acetonitrile, the net equilibria will involve CuL_2^{2+} and CuL_x^+ (x = 0–2). We thus consider the two electrode reactions 7 and 8 in addition to reaction 4. The

$$CuL_2^{2+} + e^- \rightleftharpoons CuL^+ + L \tag{7}$$

$$CuL_2^{2+} + e^- \rightleftharpoons Cu^+ + 2L \tag{8}$$

couple 7 is a combination of equilibria 4 and 5a. Hence[47]

$$E°_{298}(7) = E°_{298}(4) + 0.059 \log K_1 \tag{9}$$

Similarly we have

$$E°_{298}(8) = E°_{298}(4) + 0.059 \log (K_1K_2) \tag{10}$$

The $\bar{E}_p$ values of couples 4, 7, and 8 are given by[48]

$$\bar{E}_p(4) = E°_{298}(4) \tag{11}$$

$$\bar{E}_p(7) = E°_{298}(7) - 0.059 \log l \tag{12}$$

$$\bar{E}_p(8) = E°_{298}(8) - 0.059 \log l^2 \tag{13}$$

Since a single response is observed in practice, the interconversion of species is fast on the cyclic voltammetric time scale. The observed value is a weighted average, $E_p(av)$, given by

$$\bar{E}_p(av) = (1/a)(q\bar{E}_p(4) + r\bar{E}_p(7) + s\bar{E}_p(8)) \tag{14}$$

where $a = q + r + s$. Combining eq 9–14, we have

$$\bar{E}_p(av) = E°_{298}(4) + 0.059B \tag{15}$$

where

$$\begin{aligned} B &= (r/a) \log K_1 l^{-1} + (s/a) \log (K_1K_2 l^{-2}) \\ &= (r/a) \log (rq^{-1}) + (s/a) \log (sq^{-1}) \end{aligned} \tag{16}$$

---

(42) Apart from reported data[15,16] $E°_{298}$ values for some other ruthenium(II)–ruthenium(III) couple are as follows: $Ru(bpy)_3^{2+}$, 1.29 V; $Ru(bpy)_2L^{2+}$, 1.60 V; $Ru(bpy)L_2^{2+}$, 1.89 V; RuL_3^{2+}, 2.22 V.

(43) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.

(44) The cyclic voltammetric $\bar{E}_p$ of the copper(II)–copper(I) couple for a $\sim 10^{-3}$ M solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in acetonitrile (0.1 M in TEAP) at a scan rate of 50 mV s^{-1} is 0.987 V. The electrode reaction is quasi-reversible ($\Delta E_p = 95$ mV). A polarographic $E_{1/2}$ value of 1.00 V at the rotating platinum electrode is reported in the literature (Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852).

(45) This is implicit in an MLCT assignment of the 700-nm transition, provided the two L rings are not strongly coupled. We have also been able to isolate a complex of empirical formula CuLCl—most probably a dimer. Its spectrum (in methanol) in the 400–900-nm region is essentially the same as that of CuL_2^+ in methanol except that the intensity (per copper) is halved.

(46) Petredis, D.; Burke, A.; Balch, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 428.

(47) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1977**, *16*, 1561.

(48) Mohanty, J. G.; Chakravorty, A. *Inorg. Chem.* **1976**, *15*, 2912.

Table III.[a] Variation of Cyclic Voltammetric Peak Potentials (vs. SCE) of $[CuL_2]ClO_4$ as a Function of the Population of Equilibrium Constituents in Acetonitrile

L,[b] mL	$10^3 l$, M	$10^3 q$, M	$10^3 r$, M	$10^3 s$, M	B	$\bar{E}_p$,[c] V	$E°_{298}(4)$, V
0.00	0.2619	0.0095	0.0302	0.1159	0.905	0.775	0.722
0.05	0.3690	0.0166	0.0374	0.1016	0.598	0.767	0.732
0.10	0.4771	0.0243	0.0423	0.0890	0.388	0.762	0.739
0.15	0.5871	0.0322	0.0455	0.0778	0.235	0.751	0.737
0.21	0.7199	0.0414	0.0477	0.0665	0.107	0.741	0.735
0.30	0.9245	0.0542	0.0486	0.0528	−0.018	0.738	0.739
0.40	1.1575	0.0665	0.0477	0.0414	−0.099	0.727	0.733
0.60	1.6373	0.0856	0.0434	0.0266	−0.169	0.723	0.733
1.00	2.6281	0.1083	0.0342	0.0131	−0.187	0.722	0.733

[a] Meanings of symbols used are the same as in the text. [b] Volume of a solution (25.68×10^{-3} M) of L in acetonitrile added to a solution of the copper complex in the same solvent. The final volume is 10 mL in each case; the final copper concentration is 0.1556×10^{-3} M in each case. [c] The scan rate in each case is 50 mV s^{-1}; ΔE_p values lie in the range 100–140 mV.

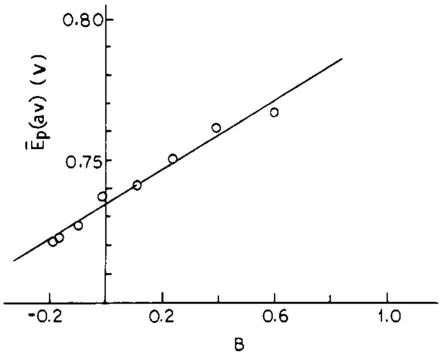


Figure 5. Variation of $\bar{E}_p$(av) with B for a solution of $[CuL_2]ClO_4$ in MeCN.

Thus the $\bar{E}_p$(av)–B plot should be linear with a slope of 59 mV and an intercept of $E°_{298}(4)$. The quantities required for calculation of B are available from equilibrium data (Table III). An excellent linear plot[49] is indeed observed (Figure 5) with a slope of 60 mV and an intercept of 0.735 V. Thus we have $E°_{298}(4) = 0.735$ V, which is 100 mV more positive than that in methanol. The results of calculation of $E°_{298}(4)$ with the help of eq 15 at each value of B are shown in Table III. Only the first entry (0.722 V) shows the expected[49] deviation; the other values span the narrow range 0.735 ± 0.004 V. With the help of eq 9 and 10, $E°_{298}(7)$ and $E°_{298}(8)$ are calculated to be 0.553 and 0.376 V, respectively.

Concluding Remarks

The azopyridine ligand system L gives stable and isolable bis complexes of both copper(I) and copper(II). The ligand acts as a good π acceptor toward copper(I), making the formal potential of the CuL_2^{2+}–CuL_2^+ couple as high as those of the most sterically hindered bis chelates of substituted 2,2′-bipyridyl[6] and 1,10-phenanthroline.[7] A good parallelism exists between ruthenium(II) and copper(I) complexes in their M–L π bonding and high metal oxidation potentials. The MLCT region of the optical spectrum of CuL_2^+ is unique in showing the t_2–e energy gap.

Acetonitrile displaces L from CuL_2^+ in two successive equilibria. The equilibrium constants are however small, showing that the affinity of copper(I) for L greatly surpasses that for acetonitrile. This is brought to a sharper focus by rewriting equilibria 5a and 6a with the inclusion of the acetonitrile (copper(I) is assumed to be four-coordinate throughout). Since pure acetonitrile is 19 M, the equilibrium constants for reactions 5a′ and 6a′ are readily calculated from

$$CuL_2^+ + 2MeCN \overset{K_1'}{\rightleftharpoons} CuL(MeCN)_2^+ + L \quad (5a')$$

$$CuL(MeCN)_2^+ + 2MeCN \overset{K_2'}{\rightleftharpoons} Cu(MeCN)_4^+ + L \quad (6a')$$

the values of K_1 and K_2 to be $K_1' = 2.31 \times 10^{-6}$ M^{-1} and $K_2' = 2.78 \times 10^{-6}$ M^{-1}. Even then dissociation equilibria proceed sufficiently to have a measurable effect on the observed potential of the copper(II)–copper(I) couple. This in turn provides a handle for controlling the potential at a specific value within a certain range by changing the concentration of the complex or of the externally added ligand.

Experimental Section

Materials. 2-(Phenylazo)pyridine was synthesized as before.[13,15] The complex $[Cu(MeCN)_4]ClO_4$ was prepared by following a known procedure.[50] The purification of solvents and preparation of supporting electrolyte for electrochemical work were done as before.[51] Dinitrogen was purified by bubbling it through an alkaline dithionite solution.

Measurements. Electronic spectra were measured with a Pye Unicam SP8-150 spectrophotometer and IR spectra (KBr disk, 4000–400 cm^{-1}) with a Beckman IR-20A spectrophotometer. Magnetic moments were measured by using a PAR vibrating-sample magnetometer (Model 155) coupled with a Walker Scientific magnet (Model L75FBAL). Voltammetric measurements were done with use of a PAR Model 174A polarographic analyzer, Model 175 universal programmer, Model RE0074 X-Y recorder and Model 377A cell system. Constant-potential coulometry was performed with the use of a PAR Model 173 potentiostat and a PAR Model 179 digital coulometer (a platinum-wire gauge was used as the working electrode). All experiments were done at 298 K under a dinitrogen atmosphere in a three-electrode configuration with a planar Beckman Model 39273 platinum working electrode. All potentials are referenced to the saturated calomel electrode and are uncorrected for the junction contributions.

For voltammetric experiments in acetonitrile the solutions were prepared in the following way. To 2 mL of a 0.778×10^{-3} M solution of $[CuL_2]ClO_4$ in acetonitrile was added a measured aliquot of a 25.680×10^{-3} M solution of L in acetonitrile, and the volume was made up to 10 mL. By varying the aliquot of L but keeping other things constant, we prepared different solutions.

Determination of K_1 and K_2. For spectroscopic determination of the equilibrium constants K_1 and K_2, solutions were pepared in a way similar to that used in the case of voltammetry. To 2 mL of an 1.132 $\times 10^{-3}$ M solution of $[CuL_2]ClO_4$ in acetonitrile were added measured aliquots of a 27.067×10^{-3} M solution of L in acetonitrile, and in each case the volume was made up to 10 mL.

From eq 5a and 6a we have

$$a = q + K_1 l^{-1} q + K_1 K_2 l^{-2} q \qquad (17)$$

The extinction coefficient of the 700-nm band was used to monitor

---

(49) The present analysis requires that the equilibrium bulk concentration of ligand should be large enough (compared to the concentration of electroactive species) to remain unperturbed by dissociation or association of L during electrolysis. On this ground the first data point of Table III is not included for the linear plot (Figure 4). Another assumption is that the diffusion of L to and from the electrode is sufficiently fast such that l is the same in bulk and at the electrode surface.

(50) Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.

(51) Datta, D.; Mascharak, P. K.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 1673.

Table IV.[a] Variation in K_1 and K_2 with Iteration

no. of iterations	10^3K_1, M^{-1}	10^3K_2, M^{-1}	no. of iterations	10^3K_1, M^{-1}	10^3K_2, M^{-1}
0	0.875	0.857	2	0.831	1.000
1	0.841	0.974	3	0.830	1.004

[a] The basic data are concentrations (a_L) of L in 10^{-3} M added externally to a $[CuL_2]ClO_4$ solution of fixed concentration (0.226×10^{-3}M). The absorbance (*A*) of the solution at 700 nm is monitored. Various a_L (*A*) values are as follows: 0.000 (0.069), 0.135 (0.081), 0.271 (0.105), 0.541 (0.131), 0.812 (0.161), 1.083 (0.189), 1.624 (0.221), 2.165 (0.232), 2.707 (0.247), 3.248 (0.255), 4.087 (0.267). The value of absorbance corresponding to the limiting situation, i.e., when there is no further spectral change on further increase of a_L, is 0.302. [b] For the zeroth iteration, i.e., for guess values of K_1 and K_2, the a_L values 2.707×10^{-3}, 3.248×10^{-3}, and 4.087×10^{-3} M were set equal to the equilibrium concentration (*l*) of the ligand.

the concentrations of the various species. The free ligand has a relatively sharp band at 446 nm, which in no way interferes with the 700-nm band. Since CuL_2^+ and CuL^+ are the only absorbing species at 700 nm, we have eq 18, where ϵ_2 and ϵ_1 are the extinction coefficients

$$d = q\epsilon_2 + K_1 l^{-1} q\epsilon_1 \tag{18}$$

$$d = q\epsilon_2 + 0.5K_1 l^{-1} q\epsilon_2 \tag{19}$$

$$(d' - 1)l^2 = (1 - d'/2)lK_1 + K_1K_2 \tag{20}$$

of the species CuL_2^+ and CuL^+, respectively, at 700 nm and *d* is the optical density (1 cm path length). With use of[45] $\epsilon_2 = 2\epsilon_1$ eq 18 transforms to eq 19. From eq 17 and 19, we have eq 20, where $d' = a\epsilon_2/d$. The plot of $(d' - 1)l^2$ vs. $(1 - d'/2)l$ should give a straight line with an intercept of K_1K_2 and a slope of K_1.

To obtain initial guess values of K_1 and K_2, we set the concentration of externally added ligand equal to the equilibrium concentration *l* when the former is large (Table IV). With these guess values of K_1 and K_2, eq 17 was solved iteratively with respect to the ligand concentration to find *q*, *r*, and *s*. The quantity $r + 2s$ gives the increment of *l* due to equilibria 5a and 6a. With use of the new corrected equilibrium concentrations of the ligand, new values of K_1 and K_2 are obtained. The whole treatment was repeated to correct *l* again and then to obtain new K_1 and K_2 values. Convergence in the values of *l*, K_1, and K_2 was achieved in three cycles (Table IV).

Preparation of Complexes. Bis(2-(phenylazo)pyridine)copper(II) Diperchlorate, $[CuL_2](ClO_4)_2$. The ligand (3.8 g) was added dropwise to 3.7 g of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 25 mL of acetonitrile with constant stirring. The yellowish green solution was then left in the air. When the volume decreased to 5 mL, the blue crystalline precipitate that deposited was filtered. The precipitate was redissolved in 10 mL of acetonitrile. To the solution was added 10 mL of benzene dropwise with constant stirring. The shining blue crystals so obtained were filtered, dried, and stored under vacuum over P_4O_{10}; yield 2.8 g. Anal. Calcd for $CuC_{22}H_{18}N_6Cl_2O_8$: Cu, 10.11; C, 42.00; H, 2.86; N, 13.36; ClO_4, 31.66. Found: Cu, 10.06; C, 42.35; H, 2.92; N, 13.54; ClO_4, 31.39

Bis(2-(phenylazo)pyridine)copper(I) Perchlorate, $[CuL_2]ClO_4$. (i) From $Cu(ClO_4)_2 \cdot 6H_2O$. The ligand (0.75 g) was added dropwise to 0.75 g of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 300 mL of 2:1 methanol–water. The mixture was boiled under reflux for 48 h. The violet solution was then evaporated on a water bath to 10 mL. A violet gummy mass is obtained. This was washed four times with 20 mL of water. The mass was then redissolved in methanol and left to crystallize. Large red-violet crystals of $[CuL_2]ClO_4$ deposited. These were collected by filtration and then dried over P_4O_{10}; yield 0.60 g.

(ii) From $[Cu(MeCN)_4]ClO_4$. The ligand (0.36 g) was added dropwise to 0.33 g of $[Cu(MeCN)_4]ClO_4$ dissolved in 100 mL of dry acetonitrile under an N_2 atmosphere with constant stirring at room temperature. The red-violet solution was stirred for 30 min more. The violet crystalline mass that separated was filtered off and was recrystallized from methanol; yield 0.27 g. Anal. Calcd for $CuC_{22}H_{18}N_6ClO_4$: Cu, 12.01; C, 49.90; H, 3.40; N, 15.88; ClO_4, 18.81. Found: Cu, 11.75; C, 49.52; H, 3.36; N, 15.73; ClO_4, 18.60.

Registry No. **(2)**$(ClO_4)_2$, 84647-93-8; **(2)**ClO_4, 84647-95-0; $[Cu(MeCN)_4]ClO_4$, 14057-91-1.

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Thin-Layer Spectroelectrochemical Evidence of Anion Binding to (Tetraphenylporphinato)iron(II) in Nonaqueous Media

K. M. KADISH* and R. K. RHODES

Received June 21, 1982

In this work, thin-layer spectroelectrochemical techniques were used to investigate the Fe(III)/Fe(II) reaction of (5,10,15,20-tetraphenylporphinato)iron(III), $(TPP)Fe^+$, as a function of counterion ($X = ClO_4^-, Br^-, OAc^-, Cl^-, F^-$) and solvent ($S = EtCl_2, Me_2SO$, py). Reduction of $(TPP)FeClO_4$ in $EtCl_2$ yields the well-known four-coordinate (TPP)Fe. However, in solutions of $(TPP)FeClO_4$ containing equimolar mixtures of Br^-, OAc^-, Cl^-, or F^- the reduction product was a mixture of (TPP)Fe and a second ferrous species. Intentional addition of excess Br^-, OAc^-, Cl^-, or F^- changed the spectra from (TPP)Fe to this second species, indicating the binding of the counterion to the ferrous center. For the F^- case, Benesi–Hildebrand plots indicate a single anion bound to Fe(II) with a formation constant of approximately 600. Anion binding does not occur in Me_2SO containing millimolar ClO_4^-, Br^-, OAc^-, or Cl^- as only $(TPP)Fe(Me_2SO)_2$ is found upon reduction. However, in excess F^-, binding does occur and the species formed is identical with the $[(TPP)FeF]^-$ observed in $EtCl_2$. Finally as the solvent is changed from neat Me_2SO to neat py, F^- is no longer able to bind to the ferrous center and only $(TPP)Fe(py)_2$ results upon reduction.

Introduction

A significant number of electrochemical studies have been carried out in nonaqueous media by using the easily synthesized iron tetraphenylporphyrin complexes. The primary motivation behind many of these studies has been to correlate the redox properties of these simple model compounds with structure–function relationships of the more complex hemoproteins.[1,2] Initial electrochemical studies with synthetic iron porphyrins in nonaqueous media have demonstrated how half-wave potentials, particularly for the Fe(III) to Fe(II) reaction, change as a function of the solvent system,[3,4] por-

---

(1) Smith, K. M., Ed. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1975.

(2) Dolphin, D., Ed. "The Porphyrins"; Academic Press: New York, 1978.

0020-1669/83/1322-1090$01.50/0 © 1983 American Chemical Society